CHARACTERIZATION OF CORES FROM THE BLACK AND MARMARA SEAS: IMPLICATIONS FOR TOC SOURCE AND PRESERVATION AND POTENTIAL FOR PALEOENVIRONMENTAL INTERPRETATION

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CHARACTERIZATION OF CORES FROM THE BLACK AND MARMARA SEAS: IMPLICATIONS FOR TOC SOURCE AND PRESERVATION AND POTENTIAL FOR PALEOENVIRONMENTAL INTERPRETATION

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Abstract

Elemental (carbon, sulphur and biogenic opal) analysis was performed on the bulk sediments recovered from four core sites (MAR00-5, MAR00-6, and MAR00-8) in the Black Sea and core site MAR98-11 in the Marmara Sea. Isotopic ($\delta^{13}C$ and $\delta^{34}S$) analysis was also performed on the bulk organic matter in the sediments. Linear extrapolations based on ^{14}C dates in the three Black Sea cores indicate that while MAR00-6 is characterized by continuous and uniform sediment deposition, cores MAR00-5 and MAR00-8 lack a record of the last ~5000 years. $\delta^{13}C$ values from ~-26‰ to ~-23‰ for the TOC in the Black Sea cores indicate the mixing of isotopically light land-derived material with isotopically heavier autochthonous carbon derived from primary marine production. Interpretations from proxy data extracted from the cores suggest that relatively higher TOC contents in core MAR00-6 compared to the other Black Sea cores can be explained by better preservation of organic matter. This is attributed to the existence of a more stable stratified water-column well below wave base and/or greater salinity contrast between surface and bottom waters at this site before 5000 yr BP.

Lithostratigraphic correlation to nearby core MAR98-12 with its ^{14}C dates places sapropel deposition in core MAR98-11 between ~9800 to ~6600 yr BP, which coincides with the contemporaneous sapropel S1 in the Aegean Sea. $\delta^{13}C$ values, the relatively high terrestrial organic-carbon component and other proxy data during this period point to a predominantly terrestrial source for the organic matter and reduced oxygen levels in the bottom waters. These data from core MAR98-11 broadly support the view of Aksu and coworkers that there has been a sustained brackish outflow from the Black Sea to the Mediterranean Sea via the intervening Marmara Sea since ~11000-10500 yr BP.

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CHAPTER ONE

1.0 Background

Organic matter in the ocean may be either of marine or terrestrial origin. Land-derived organic matter that flows to the oceans in rivers includes recently biosynthesized plant debris and dissolved humic substances accompanied by older soil humus while marine-derived organic matter is formed almost exclusively by phytoplankton within 100 meters of the ocean surface (the euphotic zone) by sunlight and the process of photosynthesis.

The vast majority of this primary production is eaten and respired somewhere within the water column during the sinking of particulate organic matter from ocean surface waters. However, a small fraction remains intact, so that the associated organic carbon is not respired to carbon dioxide and escapes being recycled in surface waters. A continuation of this particle rain over time yields a sediment record. Under ideal conditions, the sediment record can be layered, each layer representing a discrete time in the past.

Organic matter constitutes a minor fraction of marine and freshwater sediments, yet it plays a major role as an important contributor to the sedimentary record. The cycling and preservation of organic matter within the oceans are crucial steps in the global carbon cycle. This steady addition of residual carbon to marine sediments represents an important sink within the global carbon cycle. The marine carbon cycle plays a major role in controlling atmospheric carbon dioxide (CO_2) concentrations and also affects biogeochemical processes, nutrient cycling, biological availability, chemical

transport and interactions. The processes governing the formation and dissolution of this huge carbon reservoir are believed to be highly significant to climate change over geological timescales. Thus, understanding of the processes involved in the deposition and preservation of organic carbon on the sea floor is critical in the study of global climate change.

Upon arrival at the ocean floor, organic matter is further modified by a variety of processes before permanent burial. Such predepositional processes include physical transport, disturbances by organisms, chemical alteration, and dissolution. After burial, the primary composition may be altered by various diagenetic reactions.

The composition of the organic matter, the oxygen content of the bottom water, bulk sedimentation rate and the extent of bioturbation are factors that control the preservation of organic matter in the marine environment. However, unlike in oxic environments, in oxygen-depleted or anoxic environments, there is no correlation between sedimentation rate and organic carbon. In addition, oxygen deficient bottom waters do not support the existence of burrowing benthic organisms and their infaunal feeding and burrowing activities. Thus, bioturbation, which promotes the resupply of oxygen and aerobic degradation via open animal burrows, is also not an issue in anoxic environments. Sulphate reduction by anaerobic bacteria is the main mechanism for the decomposition of organic matter in anoxic environments. During this reduction process, organic carbon is metabolized by sulphate reducing bacteria (Berner, 1984).

The organic matter content of sediment is determined by the sum of the various sources and the rates at which the input is degraded by biological and chemical processes.

The processes that modify the organic matter are controlled by climatic and oceanographic factors operating during the time of production and sediment deposition.

The amounts and types of organic matter in oceanic sediments represent the residue of past biota (Meyers, 1987). This residue reflects environmental conditions that existed at different times in the past (e.g. during deposition, during diagenesis). The organic matter may therefore provide a unique record of earth's climate fluctuations and permit detection of climate signals. This record can be used to reconstruct marine and continental paleoenvironments. Efforts to extract such information from sediment studies are dependent on a thorough determination of both the type(s) (i.e. the proportion of terrestrial and marine organic matter) and amount(s) of primary organic matter preserved. The relationship between production and preservation of organic matter to paleoenvironmental changes has been reported by Arthur et al. (1988). Canfield (1994) discussed the factors influencing organic carbon preservation in marine sediments.

1.1 Introduction

1.1.1 Production of Organic Matter (Primary Production)

Marine organic matter is derived overwhelmingly from phytoplankton within the upper 100m of the sea surface. Phytoplanktons are free floating, microscopic, unicellular aquatic plants that are present throughout the photic zone of the world's oceans. Phytoplanktons come in a variety of taxonomic types (e.g., diatoms, dinoflagellates, and coccolithophores). Diatoms dominate phytoplankton blooms in the ocean, since generally they utilize nitrate more readily than either dinoflagellates or coccolithophores (Dugdale et al., 1995).

Phytoplanktons, like terrestrial plants, contain chlorophyll-a and other pigments that absorb sunlight. This is required for photosynthesis, the process which converts atmospheric CO_2 to carbohydrates and provides the energy needed for assembling organic matter from carbon dioxide and nutrients dissolved in seawater. Photosynthesis provides the ultimate source of food for marine life by converting inorganic compounds into complex organic compounds.

During photosynthesis, phytoplankton remove carbon dioxide dissolved in seawater to produce sugars and other simple organic molecules, and release oxygen as a by-product. The photosynthetic fixation of carbon by chlorophyll-containing organisms is known as primary production. Marine phytoplankton account for ~45% of global primary production. Primary production also requires an adequate and continuous supply of nutrients. The limiting nutrients are nitrogen and phosphorus. Trace elements such as iron are also required to synthesize complex molecules (e.g. proteins). The rate at which photosynthesis proceeds in marine environments is known as primary productivity.

Primary productivity thus plays a key role in the global biogeochemical cycles of carbon, oxygen, and other elements critical to both marine and terrestrial life. Factors that affect primary productivity include irradiance, temperature and nutrient availability. High surface productivity in the ocean is dependent on the rate of re-supply of the aforementioned nutrients from deeper levels in the ocean to surface waters where they can be utilized by phytoplankton.

Phytoplanktons take up dissolved carbon dioxide and fix it into organic carbon. The sinking of organic carbon out of the sunlit (euphotic) surface mixed layer acts as a

"biological pump" which effectively removes carbon out of surface layers of the oceans and sequesters it at depth and within sediments. The process by which CO_2 is incorporated into organic matter (via photosynthesis) is referred to as new or export production.

The nutrients for new production are usually supplied from below the mixed surface layer. According to Berger et al. (1989), it is this new production that fuels the export of organic matter to deeper waters and eventually to bottom sediments. This process is strongly influenced by seasonality and by episodic events.

The level of primary productivity is not, by itself, the most important control on carbon accumulation or sediment total organic carbon. Other factors such as water depth, bottom water oxygenation, sediment grain size, dilution, etc. are also important. Primary productivity however controls the character of the marine organic matter that is available and is subsequently preserved.

According to Emerson and Hedges (1988), only about 10-20% of primary production escapes the euphotic zone. Although the amount of organic carbon produced by primary productivity in the surface waters is an important variable, the proportion and amount of this material that actually reaches the sea floor is critical.

Apart from primary productivity, the composition of organic matter (OM) in the marine environment is affected by endogenous (local) and exogenous (external) factors. Such factors include heterotrophic activity, particle dynamics and circulation, and riverine and eolian inputs. Productivity gradients in overlying surface waters can affect the bottom-

water oxygen content, which in turn affects degradation and organic matter composition in the bottom sediments.

1.1.2 Preservation of Organic Matter

Preservation of organic matter in sediments depends to a large extent on the inhibition of chemical oxidation and complex mineralization processes during transport, deposition, and early burial. Early diagenesis refers to the combination of biological, chemical, and physical processes that occur during burial in the upper several hundred meters of marine sediments (Berner, 1980 b).

Decomposition of organic matter by microorganisms employs a sequential series of chemical oxidants. These oxidants, in decreasing order of thermodynamic energy yield, include oxygen, nitrate, iodate, manganese (hydr)oxides, iron (hydr)oxides and sulphate (Froelich et al., 1979; De Lange, 1986a, b). The relative importance of these oxidation processes is strongly dependent on the composition (quality) of the input material as well as on the environmental conditions prevailing before, during and after deposition. Thus, the mechanisms that determine the extent of preservation of the delivered organic material in sediments are likely to be both biologically and environmentally controlled.

Preservation of the organic matter before accumulation and burial is also influenced by several factors such as oxygen content, water-column stratification, temperature, depth and settling rate. Other factors include proximity to shore, light regime, and salinity. Many of these factors but not all are climate dependent (Tissot and Welte, 1984; Farrimond and Eglinton, 1990). Most of these predepositional factors are

also influenced by related oceanographic changes that may eventually be reflected in the organic-matter composition. These oceanographic changes might include sudden changes in primary productivity or selective preservation under different conditions.

Sedimentary organic matter is composed of many different size fractions with different degradability and settling rate. The fraction of the yearly primary production arriving at the sea floor depends on the residence time of the organic matter in the water column, which is partly controlled by water depth (e.g. Hargrave, 1973). The rate of benthic degradation is primarily determined by the flux of organic matter to the sediment. Preferential degradation of the more labile compounds occurs during sinking in the water column, horizontal transport and final burial into the sediment (e.g. Burdige and Martens, 1988; Cowie and Hedges, 1994; Wakeham et al., 1997).

At higher residence times in the water column, a larger part of the organic matter will he degraded before it reaches the seafloor. The preferential degradation of the labile compounds and benthic mineralization rate usually decrease rapidly with increasing depth in the sediment. Another major environmental control on the extent of organic matter preservation is the availability of sulphur in the form of H_2S and polysulphides.

One of the most important diagenetic processes in organic-rich marine sediments is decomposition of organic matter hy bacterial sulphate reduction (e.g. Canfield, 1989; Mossmann et al., 1991; Calvert and Karlin, 1991). In anoxic basins, contrary to what obtains in oxic and dysoxic environments, sulphate is the major electron acceptor for the oxidation of the organic matter. During sulphate reduction, hacteria utilize sulphate as an oxidant to obtain energy from organic matter with the liberation of hydrogen sulphide.

Sulphate is also utilized for bacterial respiration in anoxic environments. It has been shown that relative to aerobic respiration, approximately 75% of the energy in the consumed organic matter is transferred and stored in reduced sulphur during sulphate reduction (Howarth and Teal, 1980). When these reduced sulphur compounds are re-oxidized to sulphate, the energy is available to support bacterial growth.

Bacterial sulphate reduction produces reduced sulphur in the form of soluble sulphides (H_2S, HS^- and S^{2-}). Most of the sulphides can be partially oxidized or can react with OM and reactive metal species such as dissolved iron and iron minerals (e.g. Berner, 1984; Luther and Church, 1992). These result in the formation of metal sulphides, predominantly iron monosulphides and pyrite (FeS_2) (Berner, 1984; Howarth, 1984; Howarth and Jorgensen, 1984). Organic sulpbur compounds are also formed and stored in sediments. All these reactions may be bacterially mediated.

Iron sulphides are the most abundant metal sulphides in most sediments. The most common iron sulphide in ancient sediments is pyrite (FeS_2). Pyrite burial and oxidation link the biogeochemical cycles of oxygen, carbon and sulphur, and these processes are, next to the burial and oxidation of OM, the most important processes in controlling the oxygen levels in the atmosphere (e.g. Berner and Canfield, 1989).

1.1.3 Productivity versus Preservation of Organic Matter in Marine Sediments

Several studies have observed that nutrient-enhanced and elevated productivity coupled with the subsequent oxidation results in oxygen depletion over large areas.

Remineralization and delivery of the increased flux of organic matter to the bottom waters and seafloor is great enough to exhaust bottom water oxygen availability.

The reduced oxygen availability ultimately contributes to improving the preservation of subsequently delivered organic matter in the underlying sediments and hence organic carbon accumulation. Ample geological evidence has also been presented to support the correlation between organic matter quality and abundance and oxygen deficient paleoenvironments (Tyson, 1995).

However, the role of oxygen in the preferential preservation of organic matter and the resultant effect it has on organic richness or carbon content in sediments deposited is still a subject of controversy. This has resulted in the on-going "productivity versus preservation" debate.

Pedersen and Calvert (1990) have questioned the role of oxygen deficiency or bottom water anoxic conditions in the preferential preservation of organic carbon in sediments. They then presented an alternative argument stating that organic matter preservation is only a reflection of primary productivity (carbon flux) of the surface waters. They also suggested that sediment TOC is also controlled by many other variables such as water depth, residence times etc. that determine the flux of organic matter.

Tyson (1995) however counters that while high productivity certainly increases the probability of anoxia, anoxia does not only occur in areas of high productivity. He explained that high productivity could go largely unrecorded if the depositional environment is well oxygenated. Tyson supported his claim with the lack of correlation

between areas of high marine primary productivity observed earlier by Demaison and Moore (1980). He then concluded that oxygen deficiency occurs when the oxygen demand created by the utilization of metabolizable organic matter exceeds the rate of oxygen supply and is rather dependent on hydrographic or oceanographic factors and not solely on enhanced or high productivity.

Bralower and Thierstein (1987) also observed that sedimentological controls and preservation are generally more important than the level of primary production in the accumulation of organic matter and resulting sedimentary organic content. This view is also supported by Brumsack (1980) who stated that high productivity is not essential to produce sediments with high organic carbon (i.e. TOC values in the 0-10% range) if these can be achieved by decreasing sediment dilution and enhancing preservation by dysoxia-anoxia.

1.2 Study Area

The study area is the southwestern Black Sea and the Sea of Marmara (Figure 1.1). The two semi-enclosed basins both have well-preserved sediments that have been characterized (Aksu et al., 1995, 1999, 2000, 2002 and references therein).

1.2.1 The Black Sea

The Black Sea is an inland sea situated between 40°55' to 46°32'N and 27°27' to 41°32'E with an area of 4.2×10^5 km^2, maximum and average depths of 2200 m and 1240 m and a volume of 423,000 km^3 (Deuser, 1974).

In the Black Sea, below the layer of oxygenated surface water, oxygen is absent and hydrogen sulphide builds up in the deepwater down to a maximum of 2200 m.

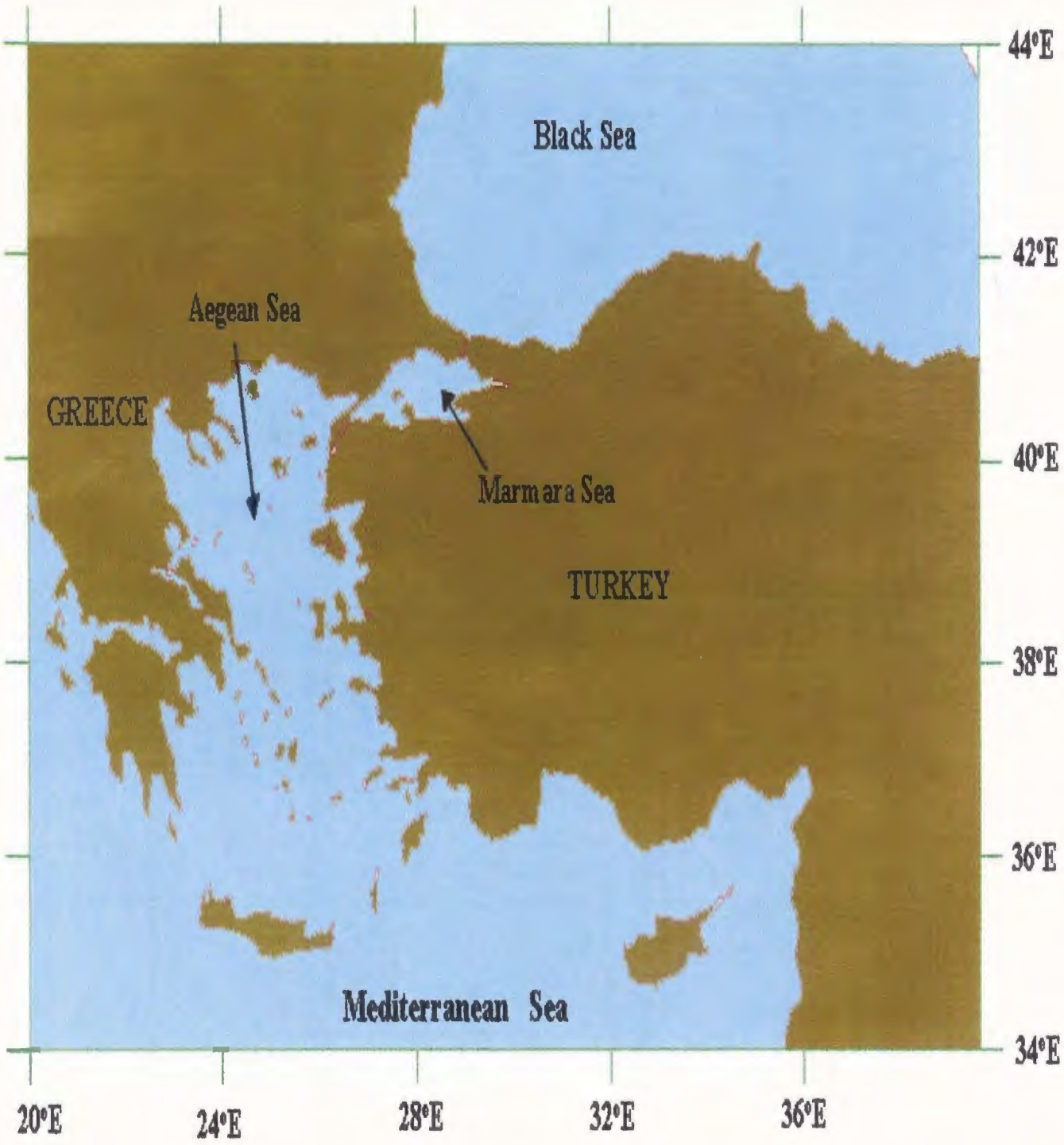


Figure 1.1: Map of study area showing the Black, Marmara, Aegean and Mediterranean Seas.

This results in ninety per cent of the Black Sea's water mass being anoxic, making it the world's largest permanently anoxic water mass. Several workers have reported the prevalence of such anoxic conditions since about 5000-7000 yr. B.P (e.g. Ross and Degens, 1974; Deuser, 1974; Calvert et al., 1987).

The Black Sea is connected to the Mediterranean Sea via the Marmara Sea and two straits; the Bosphorus and Dardanelles Straits. The Bosphorus is the narrowest strait, with an average width of 1.6 km, depth of 36 m and a total length of 31 km.

Major Eurasian rivers such as the Danube, Dniper, Dniesta, Don and Kuban, draining ~20% of central and Eastern Europe, flow into the Black Sea. These rivers show large seasonal discharge variations, and account for 76 % of the 320 km^3 annual river input into the Black Sea (Tolmazin, 1985; Özsoy and Ünlüata, 1997). A large number of smaller rivers along the Turkish and Bulgarian coasts contribute another 28 km^3 yr^{-1} to the water budget of the sea (Balkas et al., 1990). In addition, seawater flows into the Black Sea from the Mediterranean Sea via the Bosphorus strait at a rate of 200 km^3 yr^{-1} per year (Gunnerson and Özturgut, 1974: Oguz et al., 1991, 1993; Özsoy et al., 1995; Tolmazin, 1985).

The freshwater entering from rivers is less dense than seawater, resulting in stratification of the Black Sea. According to Murray et al (1989), the stratification in the Black Sea is more stable and less dependent on the seasons than in lacustrine settings. There is restricted mixing between the brackish surface and the deeper saline layers with a permanent halocline separating the two layers (Murray et al., 1991).

Various studies have been undertaken to explain the paleoceanographic evolution of the Black Sea and the eastern Mediterranean. According to Ryan et al. (1997), the Black Sea became a giant fresh-water lake during the last glacial maximum. subsequently, the post-glacial sea-level rise at ~7150 yr BP breached the Strait of Bosphorus, catastrophically re-filling the Black Sea basin with Mediterranean water. Ryan and Pitman (1999) also suggested that it was this flooding by Mediterranean waters through the Bosphorus that prevented ventilation of the deeper water column. This consequently led to a reduction of oxygen concentrations from "suboxic to dysoxic conditions" (i.e. oxygen concentrations of 0.1-1.3 ml/l O_2), and the increased preservation of organic matter.

The "*Flood Hypothesis*" proposed by Ryan and coworkers seems to contradict evidence presented by various workers, such as Gunnerson and Özturgut (1974) and Aksu et al. (1999, 2000). These workers recognized the slow establishment of two-way flow in the Bosphorus due to salinity and density differences. Surface less dense freshwater from the Black Sea was gradually replaced by more saline inflow along the floor of the strait, derived from the Mediterranean.

Aksu et al. (2002) proposed an alternative "*Outflow Hypothesis*" to explain the reconnection of the Black Sea to the Mediterranean during the last glaciation. Their hypothesis states that "the Black Sea rose to the Bosphorus bedrock sill depth by ca 11-10 ka when the Marmara Sea was ~20 m lower". Also, according to Gorür et al. (2001), the fresh-water level of the Black Sea was 18 m below the present level at 7200 yr BP and not as much as 150 m as reported by Ryan et al. (1997).

The exchange and mixing of freshwater and seawater in the upper 150 m of the Black Sea have been used to explain the anoxic conditions there. The difference in density creates a marked density boundary known as the pycnocline. The pycnocline is centred at about 50 m, where the water density increases abruptly and remains so down to the bottom 2000 m below (Ross and Degens, 1974; Deuser, 1974; Degens et al., 1978; Calvert et al., 1987). The pycnocline is the primary physical barrier to mixing and accounts for the stability of the chemocline that develops below it (Murray et al., 1989). The depth of this interface reflects, and is very sensitive to, the balance between fresh-water and salt-water inflows.

Current hydrographic conditions of the Black Sea are beyond the scope of this investigation and are described in detail by Sorokin (1983), Tolmazin, 1985, Vinogradov and Nalbandov (1990), Codispoti et al. (1991), Latif et al. (1991), and Özsoy and Ünlüata (1997).

In the deep Black Sea, marine biological production is the main sediment source. According to Yilmaz et al. (1998), the bulk of primary production at the surface of the ocean takes place in the upper photic zone (down to approximately 10% light depth) and is sustained by the influx of nutrients from the oxic/suboxic lower layers by vertical mixing which is limited due to the presence of the strong pycnocline at 50-200 m depth.

Various authors (e.g., Rohling and Gieskes, 1989; Howell and Thunell, 1992) have used enhanced organic-matter production to explain why the Black Sea is characterized by the absence of oxygen below the pycnocline and low oxygen concentrations in the pycnocline. They suggested that increased river and Mediterranean

input might have introduced additional nutrients that stimulated biological production. This may have occurred at the same time that an increased stability of the water column due to reduced vertical circulation prevented or greatly reduced formation of "intermediate- and deep-water masses" (water with normal dissolved oxygen concentrations). The result of this lack of ventilation was a basin-wide rapid depletion of oxygen concentrations caused by organic matter degradation to form carbon dioxide. This process consumed all free oxygen in the water column below the pycnocline.

Under anoxic conditions like those in the Black Sea, microorganisms use sulphate (SO_4^{2-}) for oxidation of organic material to produce hydrogen sulphide and minerals such as pyrite and iron-monosulphide. The production of toxic hydrogen sulphide makes any form of macroscopic life impossible in the water body and at the seafloor-water interface below the pycnocline.

The transport process influences the accumulation and preservation of organic material. This process is unique because of the permanent stratification in the Black Sea, the stability of its hydrographic structure and the absence of bioturbation in its bottom sediments. Hence, the Black Sea basin is a unique environment for studying changes in organic matter sources, diagenesis and preservation. The anoxic sediments have remained relatively unaltered over a long period of time and contain an excellent paleoceanographic record. These sediments can also be used to investigate the molecular and isotopic integrity of the preserved organic matter.

The geochemistry of the sediments of the Black Sea can be read as a record of profound changes in sedimentation and environmental conditions in the basin during

post-glacial sea-level rise when a connection with the Mediterranean was re-established. Geochemical characterization of the preserved organic matter in the sediments can provide insights into its origin, and post-depositional processes that led to organic matter preservation over geological time.

1.2.2 The Marmara Sea

The Marmara Sea (or Sea of Marmara) is a marine basin in northwest Turkey that is 280 km long and 80 km wide. It has a surface area of 11,500 km^2 and a maximum depth of 1238 m (Yanko et al., 1999). The Sea of Marmara serves as the link between the Black Sea and the Aegean Sea. It is connected to the Black Sea on the east through the Bosphorus Strait (~40 m deep), and the Aegean Sea on the west by the Dardanelles (or Çanakkale) Strait (~70 m deep). The Aegean Sea leads to the eastern Mediterranean (Figure 1).

As a result of its position between the Aegean and Black seas, the Marmara Sea is of oceanographic importance as it is influenced by environmental conditions in these adjoining seas. Since it serves as a gateway between two larger seas of contrasting character, the small waterway and linked straits are referred to as the "Marmara Sea Gateway".

According to Beşiktepe et al. (1994), satellite altimetry data show that the surface of the Black Sea is, on average, 30 cm (±10 cm) above the level of the Marmara Sea while Bogdanova (1969) had earlier observed that the Marmara Sea is approximately 5–27 cm above the level of the northern Aegean Sea. The resulting elevation differences drive the net outflow into the Aegean Sea via the Straits of Bosphorus and Dardanelles.

The two narrow and shallow straits also permit and control the amount and style of water exchanged between the Mediterranean and Black seas.

The Marmara Sea is occupied by two distinctly different water masses (Latif et al., 1992). These are a brackish-water mass (with salinity of 22-26$^{o}/_{oo}$) of Black Sea origin forming a relatively thin, cooler (5–15° C) upper surface layer (10-15m thick). This well oxygenated upper layer is separated from the warmer (15–20° C), deep waters of Mediterranean origin (with 38.5-38.6$^{o}/_{oo}$ salinity) by a sharp interface (pycnocline /halocline) about 10-20m thick (Tuğurl and Polat, 1995; Ergin et. al., 1994).

The water column stratification, together with the topographic restriction of the Bosphorus and Dardanelles straits, prevents the efficient circulation of the sub-halocline layers (Çağatay et al., 1999). The permanent pycnocline/halocline also drastically limits ventilation resulting in decreased dissolved oxygen content of the bottom waters.

In the Marmara Sea, the water is permanently deficient of oxygen below the pycnocline/halocline despite the supply of oxygen-rich marine water through the Dardanelles strait (Beşiktepe et al., 1994). However, the continuous supply of oxygen prevents anoxic conditions like in the Black Sea. The circulation and hydrographic conditions of the Marmara Sea are described in detail by Beşiktepe et al (1994).

In the Marmara Sea, photosynthesis is reportedly limited to the upper layer, including the interface between 15 and 30 m while nutrient and organic carbon concentrations of the sub-halocline waters show much less seasonal variation than in the outflow from the Black Sea (Başturk, et al., 1988). In terms of the ingredients for primary

production, the basin is dominated by inputs both from natural sources (input from the sub-halocline waters by vertical mixing and the Black Sea inflow) and land-based sources. The Biga, Gonen and Kocasu rivers are the only rivers flowing into the Marmara Sea (Çağatay et al., 1999). These rivers are responsible for input of nutrients and allochthonous organic matter to the southern shelf of the Marmara Sea.

The paleoceanographic evolution of the Marmara Sea is clearly controlled by the two adjacent water bodies. Earlier studies have reported that during the Quaternary glacial periods, the Marmara Sea was a freshwater lake that was isolated from the Aegean Sea (Stanley and Blanpied, 1980; Smith et al., 1995). The Marmara Sea later became reconnected to the Aegean Sea during the interglacial sea-level rises, which allowed the in-flow of Mediterranean water mass into the Marmara Sea via the Dardanelles Strait and then into the Black Sea as the shallower Bosphorus sill depth was breached (Aksu et al., 1999; Çağatay et al., 1999, 2000; Hiscott et al., 2002). This simple scenario is only possible since the time of the oxygen isotopic stage 2 (~12000 yr BP). Before that time, even when global sea level was low, the Marmara Sea was not isolated from the Aegean Sea because the Dardanelles Strait was wide and was ~13.5 m deeper than today (~70 m). This would have allowed limited water exchange between the Aegean Sea and the Marmara Sea during earlier glacial maxima (Yaltirak et al., 2000).

Sedimentary records from the Sea of Marmara provide a key to understanding interactions between the Black Sea and the Mediterranean Sea. It is believed that the history of paleoceanographic interaction between the Marmara Sea and the two adjoining

seas as well as water flow directions between them is preserved in their bottom sediments (Aksu et al., 1999; Çağatay et al., 1999).

The paleoceanographic and hydrographic interactions described above are believed to be related to climatic control and paleoenvironmental conditions, particularly the events that took place during the last glacial to Holocene transition. However, controversy still surrounds the exact nature and causes of these paleoceanographic and hydrographic interactions. The controversy is particularly intense especially with regard to the way in which the Bosphorus Strait was breached and the genesis of organic-rich sediments in the region.

1.4.2 Sapropels

Various studies (e.g., Calvert, 1983; de Lange et al., 1989) have reported the occurrence of organic-rich sediments in the eastern Mediterranean basin. These organic-rich layers are >1cm thick and have >2% organic carbon. They are called sapropels. Layers having similar thickness and 0.5-2% organic carbon are termed sapropelic (Kidd et al., 1978).

The deposition of sapropels and the attendant increase in organic-matter concentrations in the eastern Mediterranean have been attributed to cyclic changes in environmental conditions (e.g., Sigl et al., 1978; Calvert, 1983; de Lange and ten Haven, 1983). Such conditions include basin-wide stagnation due to density stratification caused by large influxes of freshwater during inter-glacial melting periods. Periods of increased flux of organic material due to enhanced organic-matter production in the surface waters

and/or preservation under anoxic/oxygen-deficient conditions (Pedersen and Calvert, 1990) have also been cited. Aksu et al. (1995a, b), however, did not find much evidence for enhanced primary productivity during sapropel deposition (sapropel S1) but rather found indications of deposition during intense reduction in surface-water salinities.

The organic-rich sediments are important indicators of paleoceanographic conditions in the Marmara Gateway. Carbon-isotopic observations made by Abrajano et al. (2000) on several cores from the Black and Marmara seas have provided major insights into the paleoenvironments and organic-matter sources for the formation of sapropel M1. Their findings are consistent with earlier suggestions of limited atmospheric CO_2 input due to water-column stratification, and increased respired CO_2 input as a result of major freshwater outflow from the Black Sea into the Marmara Sea through the Bosphorus, consistent with Aksu et al. (1995).

It is also believed that sapropel layers mark rhythmic changes in the physical, chemical, and biological conditions of the Mediterranean Sea (de Lange and ten Haven, 1983). Sediment records from the thesis area may be helpful in identifying the controls on organic-matter accumulation and their relative importance.

1.3 Project Goals and Objectives

The Marmara Sea Gateway has experienced profound environmental and oceanographic changes during the last several million years. The Black Sea and the adjacent Sea of Marmara, as isolated marginal seas, react in a particularly sensitive way to paleoenvironmental changes. Sedimentary sequences in the area are also strongly affected by sea-level changes as in all seas.

It is widely acknowledged that evidence for profound changes in the climate and oceanography of the Marmara Sea Gateway can be found in bottom sediments of the Black and Marmara seas. It is also widely believed that changes in paleoenvironmental conditions cause cyclic changes in the total amount and composition of sedimentary organic carbon preserved in these sediments.

Thus, a record of organic-matter inputs, depositional environmental conditions and organic-carbon preservation can be important for interpreting paleoenvironmental conditions. This may provide important clues to the palcoclimatic and paleoceanographic evolution of this region. However, despite an ever-increasing literature and various geological investigations on the Marmara Sea Gateway, there are still considerable uncertainties regarding its late Pleistocene and Holocene geological and environmental history. Aksu et al. (2002) stated that their alternative "*Outflow Hypothesis*" best explains the "seismic, and fossil data in the Marmara Sea Gateway". They claim to have disproved Ryan et al. (1997)'s earlier hypothesis, which they have since referred to as the "*Flood Hypothesis*", for the reconnection of the Black Sea to the Mediterranean during the last glaciation. However, Aksu et al. (2002) acknowledged the need for more studies to thoroughly evaluate the gateway's late Quaternary history.

Similarly, the depositional processes and climatic conditions that resulted in the deposition of organic-rich sediments and sapropel layers through geological time in the eastern Mediterranean also remain uncertain (Aksu et al., 1995; Cramp and Sullivan, 1999), in spite of three decades of research. There is a strong need for elucidating the origin, compositional changes and environmental conditions leading to the formation and

preservation of organic-rich sediments from the Black and Marmara seas. In particular, the chronology of paleoclimatic and paleoceanographic events as well as the sedimentary and geochemical consequences associated with climate and sea-level changes in the Black Sea and Sea of Marmara during the last glacial-interglacial transition need to be elucidated. These events are believed to have strong paleoenvironmental implications for the Black Sea and Marmara Sea basins and the eastern Mediterranean as a whole.

The goals of this project are to investigate the sources, composition and preservation of organic matter in sediment cores collected in 1998 and 2000 from the Marmara Sea Gateway. Complementary existing data on elemental, isotopic and biogenic signals will be utilized as depositional, paleoclimatic and paleoceanographic proxies. The new data presented in this thesis will be related to paleoenvironmental changes with a view to proffering a plausible reconstruction of past climatic and environmental history of the study area. The implications for the origin and formation of sapropels throughout the eastern Mediterranean will also be discussed.

1.3.1 Approach and Specific Project Objectives

Sediment cores from the Black and Marmara seas will be analyzed using stable-isotopic geochemical techniques. Various geochemical proxies such as concentrations of elemental carbon, sulphur, and biogenic silica will also be utilized, as will bulk carbon and sulphur isotopic data.

The objectives are to address the following questions:

- How do the principal sedimentary components of organic matter in the sediments vary in quantity and character?

- What are the contributions of terrestrial versus marine organic matter to total organic carbon (TOC) in these sediments?
- What is the relationship between organic-carbon composition and sources of the organic matter?
- What isotopic variations are found in the sediments, and what is their paleoceanographic and depositional significance?
- What implications do changes in the isotope signals of carbon and sulphur have in terms of source, composition and preservation of organic matter in the sediments? What are the main controls on organic richness in the sediments (e.g., elevated plankton productivity or, alternatively, enhanced preservation)?
- What role does sulphur play in the deposition and preservation of organic matter in the sediments?
- How can changes recorded in the sediment record of the Black Sea and the Sea of Marmara be correlated to hydrologic and geochemical event(s) and interaction(s) between the two seas?
- What is the potential for making paleoclimatic and paleoenvironmental deductions from the elemental and isotopic information obtained from this study?
- Can results obtained from this study shed light on issues of sapropel formation, and the paleoceanographic and climatic evolution of the Marmara Sea Gateway and/or the eastern Mediterranean?

Chapter Two

2.0 Materials and Methods

Geologists use a variety of indirect measures referred to as proxies to delineate past environmental conditions. These proxies contain indicator signals that reflect conditions of original deposition or some other syndepositional property. The proxy indicators are used to estimate a wealth of different characteristics or conditions such as water temperature, oxygen content, salinity as well as production, destruction and preservation of organic material, leading to better understanding of paleoclimatic and paleoceanographic evolution of an area. The list of proxies used in the earth sciences is very long indeed and several geochemical proxies are routinely used for the reconstruction of oceanographic conditions in the geological past. These geochemical proxies respond systematically to changes in important, but immeasurable variables, and can therefore be used to reconstruct physical and chemical parameters that prevailed during deposition.

2.1 Present Study

This thesis involves the geochemical characterization of sediments using elemental and stable isotopic data to determine the sources of, and the preservation of, organic matter in five cores collected from the Marmara Sea and the southwestern continental shelves of the Black Sea. To achieve the study goals and objectives set out in Chapter 1, the chronologies of the cores and a suite of geochemical parameters (proxies) such as total organic carbon (TOC), total sulphur (TS), $\delta^{34}S$ and $\delta^{13}C$ composition were determined. These were then combined with a characterization of surface water

productivity based on chemical extraction procedures involving the analysis of the biogenic silica (opal) content.

Three Black Sea cores labelled MAR00-5, MAR00-6, MAR00-8 and a Marmara Sea core labelled MAR98-11 were analyzed in this study. An additional core from the Marmara Sea cores labelled MAR98-12 had been analyzed previously by Abrajano et al. (20022) and Hiscott and Aksu (2002). This chapter describes in detail the sample preparation techniques for the required elemental and isotopic analyses as well as the analytical scheme utilized.

2.2 Samples

Samples used in this thesis were obtained from five 120–220 cm-long gravity cores collected from the southwestern Black Sea and the Marmara Sea during the 1998 and 2000 cruises of the research vessel *Koca Piri Reis* of the Institute of Marine Sciences and Technology. The cores were collected using a 4 m-long corer with 10 cm internal diameter and a 400 kg weight. The core sites (Figure 2.1) were carefully selected using ~7500 line km of high-resolution boomer profiles and 40 cubic-inch sleeve gun profiles located by satellite navigation (GPS). Core length, water depth, latitude and longitude coordinates for the five gravity cores with two depth intervals are given in Table 2.1.

The cores were shipped to Memorial University of Newfoundland where they were carefully split, and cleaned. Photography of split cores documents changes of sediment color and texture that are often important indications of various paleoenvironmental and paleoceanographic changes. The fresh exposed surfaces of the split and cleaned cores were photographed and then described. Sediment color was determined using the Rock-Color chart published by the Geological Society of America.

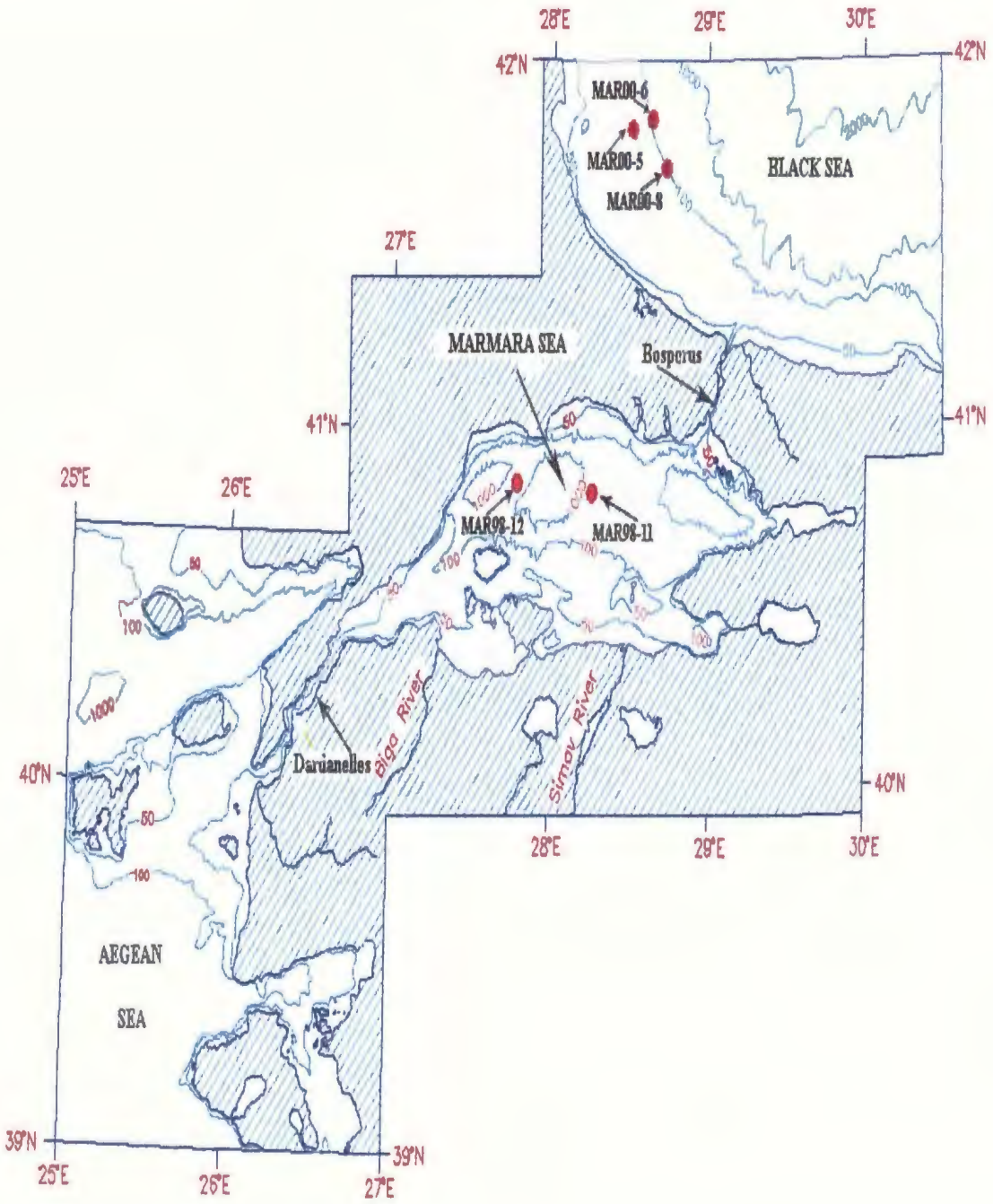


Figure 2.1: Location map of study area showing the coordinates and site position of the studied gravity cores (discussed in the text) collected in the southwestern Black Sea and the Marmara Sea during the 1998 and 20000 cruises of the research vessel *Koca Piri Reis* of the Institute of Marine Sciences and Technology, Dokuz Eylül University, Turkey. Isobaths (50,100 and 1000) are in meters.

Core #	Depth (cm)	Latitude	Longitude	Water Depth (m)
MAR00-5	175	41°49.01'N	28°30.68'E	-83
MAR00-6	131	41°50.38'N	28°37.54'E	-127
MAR00-8	180	41°42.16'N	28°43.32'E	-96
MAR98-11	227	40°50.07'N	28°27.63'E	-651
MAR98-12	216	40°50.54'N	27°47.68'E	-549

Table 2.1: Core length, water depth, longitude and latitude coordinates of five gravity cores considered in this study (modified from Aksu et al., 2002).

2.3 Core Descriptions

The sedimentary facies present in gravity cores from the Black Sea and the Sea of Marmara vary from marginal marine sands and deltaic deposits to hemipelagic muds and organic-rich sapropels (Hiscott and Aksu, 2002). Hiscott and Aksu (2002) subdivided the stratigraphy into three allostratigraphic units (cf. Walker, 1992), A, B and C, using as boundaries subaerial unconformities and their correlative conformities, flooding surfaces and radiocarbon dates.

Hiscott and Aksu (2002) defined Unit A as extending from the seafloor downwards to a ~12 ka (thousands of years before present; 12000 yr BP) sequence boundary that is an unconformity in modern water depths less than ~100 m, and a correlative conformity in deeper areas. Allostratigraphic Unit B was identified as being present only at water depths greater than ~100 m in both the Black Sea and Marmara Sea. The unit represents basinal or prodeltaic deposition during the 23-12 ka lowstands of oxygen isotopic stage 2. Unit C with an age of ~23.5-29.5 ka was also identified in the Marmara Sea as a laminated sapropel (M2: ≥2% TOC, Kidd et al., 1978) like Subunit A2 of Abrajano et al. (2002). Furthermore, Hiscott and Aksu (2002) observed that these allostratigraphic or "allounits", when traced from shelf to basin, provide "the opportunity to reconstruct paleoenvironmental, paleogeographic and paleoceanographic conditions" of the Marmara Sea gateway.

2.3.1 Black Sea Cores

In the Quaternary succession of the Black Sea, allounits A and B as described above have been identified. However allounit B that represents deltaic deposition during

the last glacial maximum has not been cored. Summary of allostratigraphy, lithologies and radiocarbon ages in the Black Sea cores is presented in Figure 2.2.

2.3.1.1 Core MAR00-05

Core MAR00-05 (~ 175 cm long) was collected near the present-day shelf edge of the southwestern Black Sea at ~ 83 m water depth (Figure 2.1). The core recovered an approximately 165 cm-thick interval of moderately burrowed olive gray mud with rare shells, interrupted by a 10 cm-thick burrowed mud with many scattered shells at 75-85 cm depth in the core (Figure 2.2). The 168-175 cm interval is a sand-bearing silty mud deposit with abundant (~ 30%) shells (Aksu et al., 2002).

2.3.1.2 Core MAR00-06

Core MAR00-06 was collected at ~ 127 m water depth from the seaward slope of the shelf-edge deltas in the southwestern part of the Black Sea (Figure 2.1). The total recovered length of the studied core is 131 cm (Figure 2.2). The core recovered ~ 49 cm of color-banded greenish-gray and black muds, overlying 82 cm of greenish-gray mud with scattered shells and shell-rich layers (Aksu et al., 2002).

2.3.1.3 Core MAR00-08

Core MAR00-08 was collected at the toe of the present-day shelf edge of the southwestern Black Sea. The core is 180 cm long and the water depth of this site is about 96 m (Figure 2.1). The core recovered a 126-cm-thick veneer of moderately burrowed greenish-gray muds, with frequent shells, and shell-rich layers.

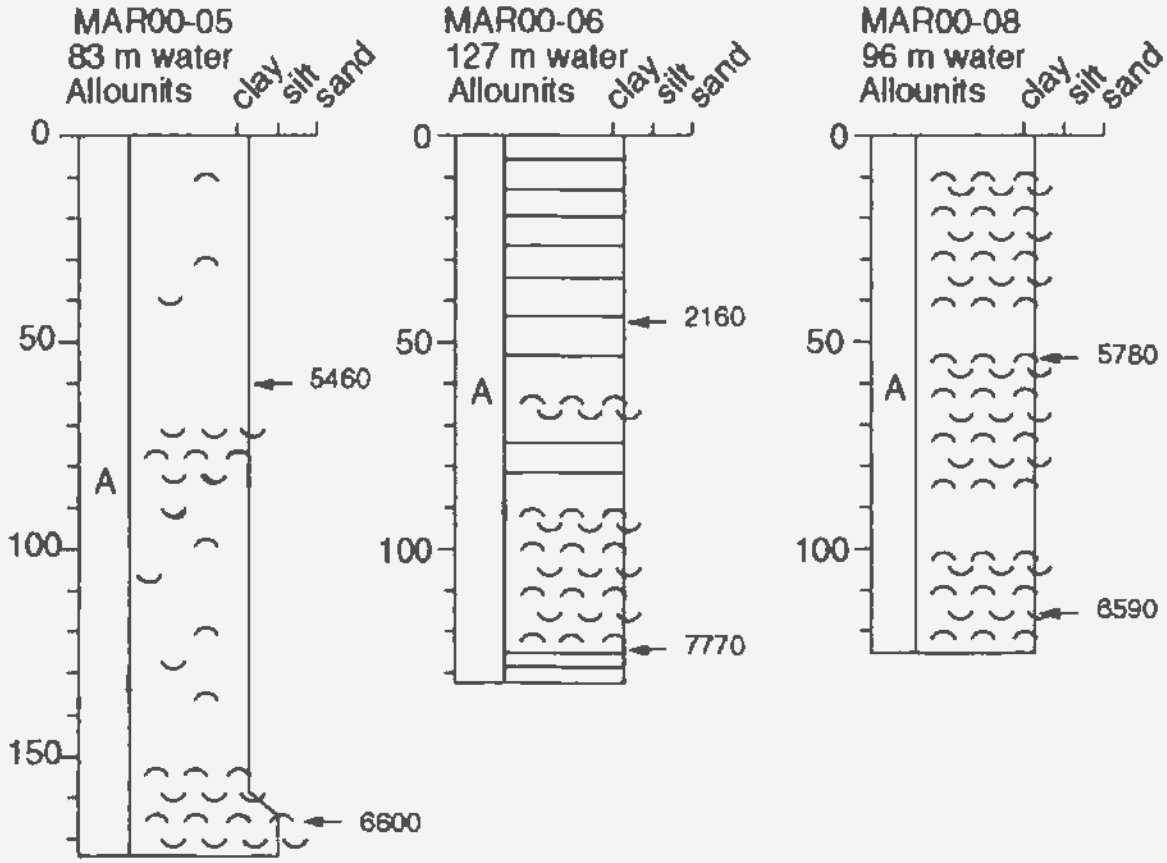


Figure 2.2: Summary lithologies, allounits and radiocarbon ages in Black Sea cores MAR00-05, MAR00-06 and MAR00-08. Allounits are described in Hiscott and Aksu (2002). Arrows with numbers indicate radiocarbon ages in yr BP.

2.3.2 Marmara Sea Cores

Two Allounits, A and B, were identified in cores MAR98-11 and MAR98-12 (Hiscott and Aksu, 2002). Unit A is divided into two subunits in Marmara Sea cores: A1 (~0-6 ka) and A2 (~6-12 ka). Subunit A2 represents a laminated sapropel deposit (M1) in deep basins (Abrajano et al., 2002). Summary of allostratigraphy, lithologies and radiocarbon ages in cores MAR98-11and MAR98-12 as described by Hiscott and Aksu (2002) is presented in Figure 2.3.

2.3.2.1 Core MAR98-11

Core MAR98-11 (~ 227 cm long) was recovered from a saddle between deep basins of the eastern and central Marmara Sea at a water depth of 651 m (Figures 2.1 and 2.2). Tbe upper 108 cm interval consists of light olive gray (Munsell 5Y5/2) grading to a slightly darker olive gray (Munsell 5Y4/2) mud with no shells or shell fragments. Monosulphide streaks begin approximately around 50 cm depth, increasing in frequency with depth. The sapropel layer from 108 cm to 185 cm consists of laminated dark gray silty mud. The upper 108 cm to ~147 cm interval is characterized by silty mud that is color mottled from a light olive gray (Munsell 5Y5/2) to darker olive gray (Munsell 5Y4/1), back to light olive gray. The interval is also bioturbated and mottled with monosulphides. From 147 cm to 185 cm, mm-scale discontinuous silty laminations, accentuated hy color banding (probably varved), bioturbated and mottled with monosulphides were observed. The color in this interval range from olive gray (Munsell 5Y5/2) to darker olive gray (Munsell 5Y4/1) to olive black (Munsell 5Y2/1) laminated sediments. From 185 cm to 217 cm, there is a color change back to light olive gray (Munsell 5Y5/2) silty mud with few laminations and iron monosulphide mottles between

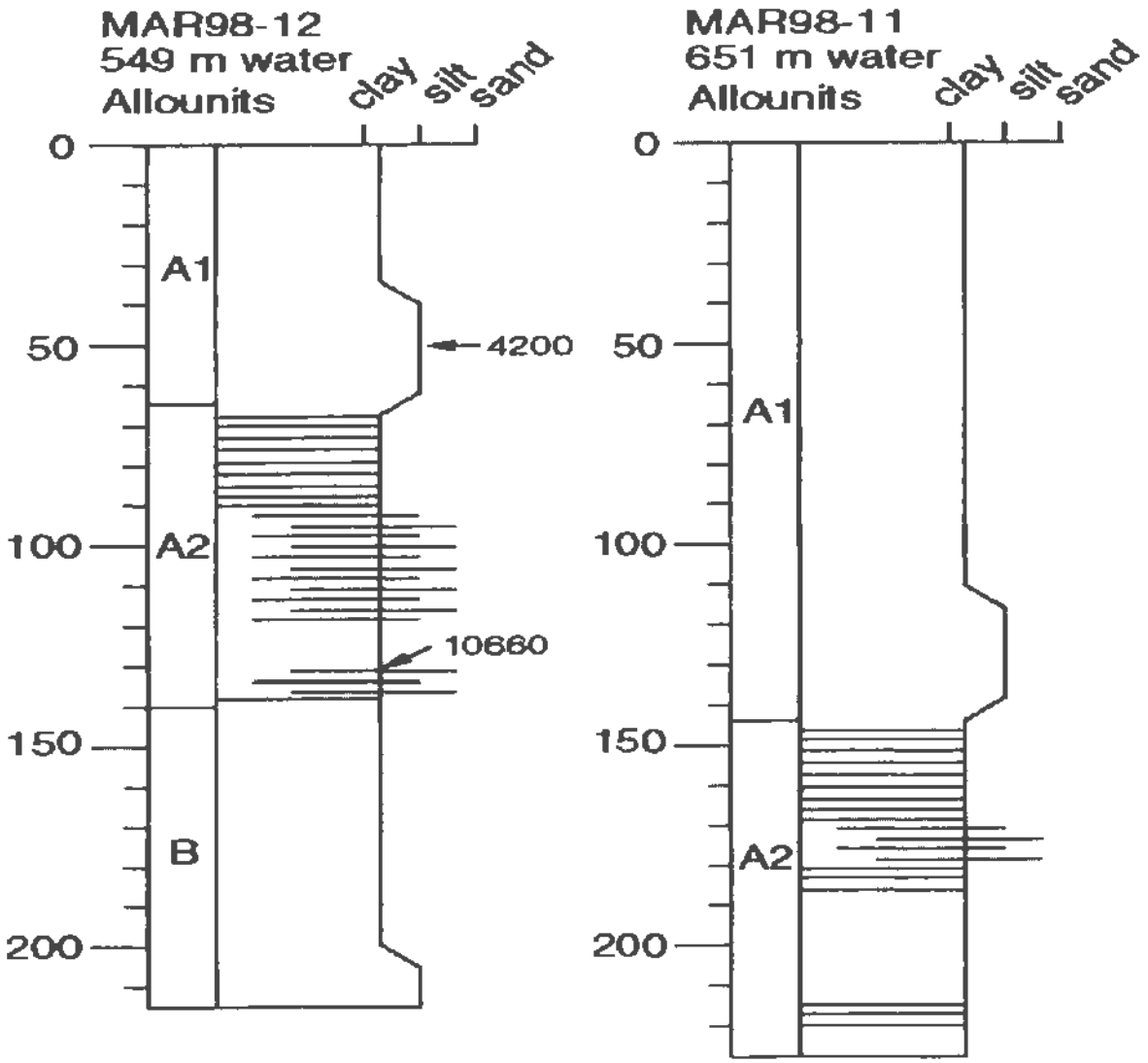


Figure 2.3: Summary lithologies, allounits and radiocarbon ages in Marmara Sea cores MAR98-11 and MAR98-12 described by Hiscott and Aksu (2002). Arrows with numbers indicate radiocarbon ages in yr BP.

between 208 and 217 cm. Thereafter, there is a marked change to 218 cm, where there is a 1 cm band of olive black (Munsell 5Y2/1) monosulphides followed by ~1 mm band of broken shell fragments. The 219 cm to 227 cm interval (the base of the core) consists of a light olive gray (Munsell 5Y5/1) layer with frequent monosulphides.

2.3.2.2 Core MAR98-12

Core MAR98-12 (~ 216 cm long) was recovered from the western saddle of the deep Marmara Sea at a present-day water depth of 549 m. Unit A in core MAR98-12 consists of dark yellowish brown muds with the sand fraction almost entirely biogenic, consisting of foraminifera, gastropods and bivalves while the silty clay fraction contains notable quantities of coccoliths (Aksu et al., 2002a). Subunit A2 consists of much darker (olive black) silty/clayey muds, is unburrowed, and displays distinctive faint parallel lamination/bedding, and color banding. The TOC values in this basinal core exceed 2.4% in the upper portion of Subunit A2 (Abrajano et al., 2002). Thus, Subunit A2 is partly a true sapropel (>2.0% TOC) and partly a sapropelic layer (0.5-2.0% TOC) according to the definition of Kidd et al (1978). Unit B in core MAR98-12 consists of light olive gray silty muds and bioturbated muds with iron monosulphide mottles.

2.4 Sampling Procedure

2.4.1 Sample Extraction

Sediment samples were extracted from the centre of the split-core surface to the outer edge of the core using a clean sampling spatula. Approximately 20 cm^3 of wet sediment was removed at ~ 10 cm intervals from each core. The sediments were then put into aluminum foil cups and dried in a fume hood at room temperature for a few days.

The dried samples were subsequently stored in glass scintillation vials, and properly labelled.

2.4.2 Sample Preparation

Sample preparation is as important as an actual measurement on the sample as any processing might affect the overall result.

Sample preparation starts with sample homogenization. The dried samples were ground to <250 μm or less using a mortar and pestle. Thorough sample homogenization in the grinder stage is required, to make certain that the tiny sub sample taken for analysis is representative of the total sample. Poor precision can often be traced to inadequate grinding that leaves fibrous matter or visible granules in the sample. A 5g portion of each sample was weighed out after grinding to achieve a uniform sample. Each powdered sample was then poured into a plastic test tube to which 5 ml of water was added to wet the sample before the acid treatment. Carbonates were removed by the addition of 20 ml of 50% v/v HCl. The acidified sample was allowed to sit overnight in the fume hood. The following day, pairs of test tubes were matched by weight using a balance. The pairs were centrifuged at 1500 rpm for three minutes in an IEC HN SII centrifuge. Once the centrifuging process was complete, the samples were repeatedly washed to neutrality with distilled water. The samples were then dried overnight in an oven set at ~25°C, after which they were homogenized again using an agate mortar and pestle before being sealed in 5 x 9 mm tin sample capsules ready for analysis.

2.4.3 Analytical Scheme of Sample Analysis

The strategy employed for analytical treatment of sediment samples is shown schematically in Figure 2.4.

2.5 Analytical Techniques

Each sediment sample from four of the gravity cores was analyzed for total organic carbon (TOC), total sulphur (TS) and biogenic silica (opal) content, as well as the stable carbon ($\delta^{13}C$) and sulphur ($\delta^{34}S$) isotopic composition of bulk organic matter. Only TOC, $\delta^{13}C$ and biogenic silica (opal) content were determined previously in core MAR98-12 samples by Abrajano et al. (2002).

2.5.1 Isotope Ratio Mass Spectrometry

The isotopic composition of a sample is measured by determining the ratios of the stable isotope masses being examined. In the case of this study, the ratios are $^{13}C/^{12}C$ and $^{34}S/^{32}S$. These ratios are measured on an isotope ratio mass spectrometer (IRMS), a device that separates ions of the element of interest on the basis of their differing mass/charge ratio (m/z). However, unlike other conventional mass spectrometers, the instrument has been specifically designed to measure the proportions of particular isotopes.

2.5.1.1 Principle of operation of the IRMS

The mass spectrometers used for isotopic analysis generally comprise three basic sections: an ion source, a mass analyser and an ion collection assembly (Figure 2.5).

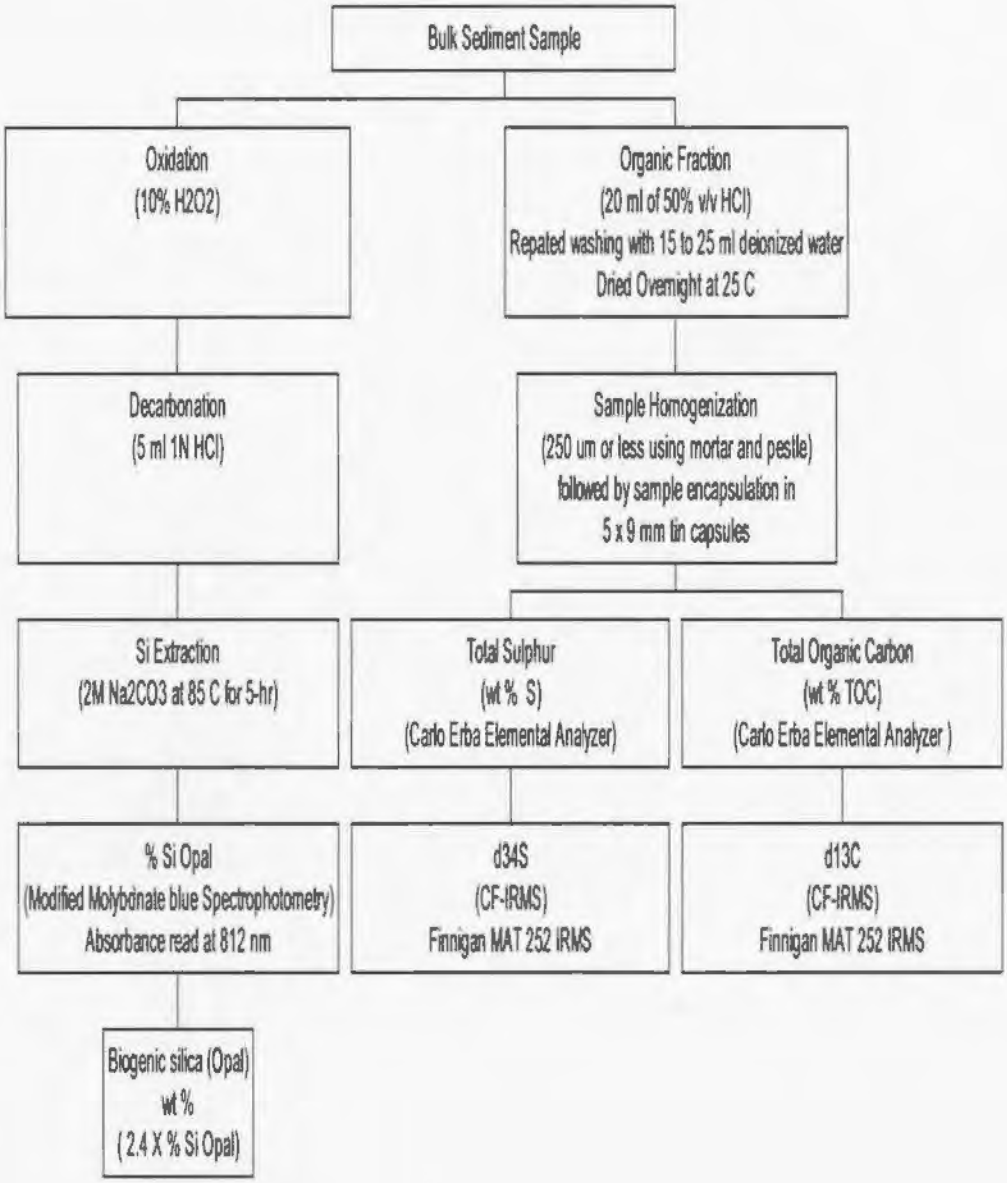


Figure 2.4: Analytical scheme for elemental and isotopic analysis of sediment samples

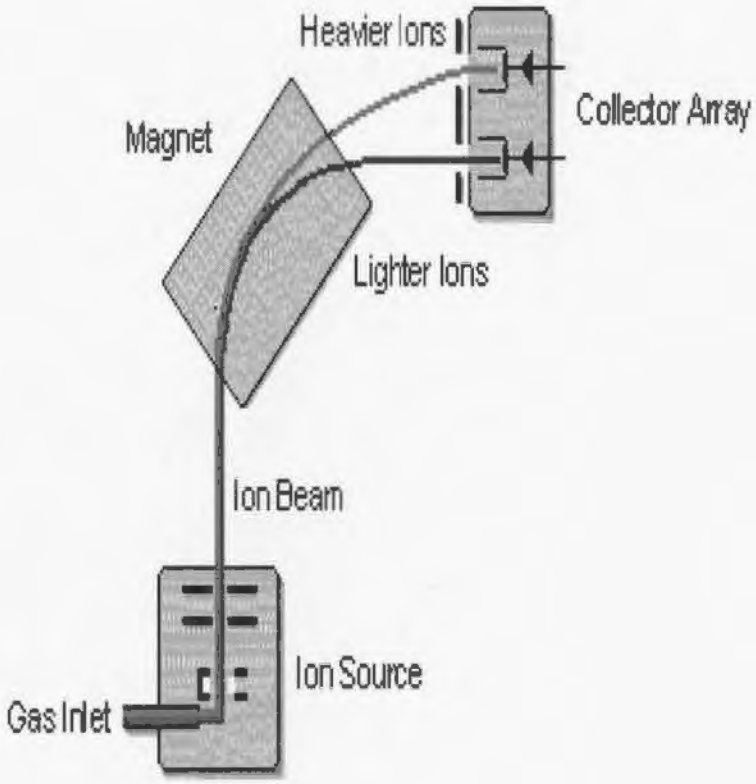


Figure 2.5: Simplified diagram of an isotope ratio mass spectrometer (Modified from Meier- Augenstein, 2002).

Gaseous molecules (CO_2 for carbon isotopes; SO_2 for sulphur isotopes) are introduced into the ionisation chamber where interaction with a focused electron beam causes electrons to be stripped from the molecules resulting in the formation of positive ions. The ions are then accelerated out of the chamber down a flight tube and enter a strong magnetic field created by an electromagnet, where they are separated according to their mass-to-charge ratio (m z). Ions in the field are deflected into circular paths whose radii are proportional to their masses. Thus, lower mass ions are deflected more and higher mass ones less. The result is that the ion beam is divided into its component masses, which are typically collected by a simple collector array consisting of three or more Faraday cup collectors. The impact of the ions is translated into a recordable signal that is collected for data processing and analysis. The absolute levels of the signals depend on the amount of gas, which is admitted into the ion source. The critical value is the ratio of the signals falling into the different collector cups (Meier-Augenstein, 2002)

In order to carry out IRMS analysis, the analyte (i.e. the solid or liquid material which is to be analyzed) must be converted into a simple gas isotopically representative of the original sample, as only pure gases, e.g. SO_2, CO_2, or pure gas contained within a carrier gas can be analyzed. The particular gas that is to be analyzed (SO_2 and CO_2 in this study) is then isolated before entering the ion source of an IRMS.

An elemental analyzer is an automated sample preparation instrument in which samples are converted into pure gases via combustion, reduction, and pyrolysis reactions in the presence of catalysts. Two main types of preparation are widely employed to convert solid, liquid and gaseous samples into pure gases for analysis in the IRMS: Continuous Flow and Dual Inlet. The former was utilized in this thesis.

2.5.1.2 Continuous Flow

In continuous flow analysis, sample preparation, and subsequent analysis, is carried out on-line in a continuous flow of helium carrier gas. The sample is introduced into a helium stream from one of several peripheral devices. A capillary takes a sample of the Helium stream and introduces it into the mass spectrometer.

2.5.2 Elemental and Bulk Isotopic Analyses

TOC and TS as well as $\delta^{13}C$ and $\delta^{34}S$ were measured in this study using Continuous Flow Isotope Ratio Mass Spectrometry (CF-IRMS). The CF-IRMS system at Memorial University of Newfoundland (MUN) consists of an online analytical system combining an isotope ratio mass spectrometer (Finnigan MAT 252) and an elemental analyzer — a Carlo Erba CNS elemental analyzer (NA1500) with an automated on-line dry combustion method. The combustion furnace was operated at 1000°C, and the reduction oven was operated at 650°C.

2.5.2.1 TOC and $\delta^{13}C$ Analysis

The amount of TOC and its carbon isotopic composition were determined in each sediment sample at the Stahle Isotope Laboratory at MUN using a Carlo-Erba A 1500 Elemental Analyzer coupled to a Finnigan MAT 252 triple collector isotope-ratio mass spectrometer (IRMS) via a Finnigan MAT Conflo II split interface.

Procedure: Sub-samples of dry sediment were acidified using 50% HCl. The carbonate-free residues were then dried overnight in an oven at ~25°C. A small amount of sample (~15 mg) was transferred into 4 x 6 mm capsules, which were then carefully sealed using

two forceps for elemental TOC analysis. TOC was converted to CO_2, H_2O and other oxidized gases in the oxidation chamber and then passed through a reduction reagent (to remove excess O_2), a $Mg(ClO_4)_2$ water trap and a 1.2-m Poropak QS50/80 chromatographic column at 70°C for final isolation. TOC quantification from measurement of generated CO_2 was accomplished using an external standard (sulfanilamide, $C_6H_8N_2O_2S$) and a thermal conductivity detector (TCD). The TOC concentration in the samples was then back calculated as weight percentage of the dry weight of the sediment.

For carbon isotopic determination on the total organic carbon, the generated CO_2 was then carried from the TCD by Helium gas to a ConFloII interface, which allows a portion of the Helium and combustion gases to enter directly into the ion source of the IRMS.

2.5.2.2 Total Sulphur (TS) and $\delta^{34}S$ Analysis.

The Carlo-Erba A 1500 Elemental Analyzer coupled to a Finnigan Mat 252 isotope-ratio mass spectrometer (IRMS) at MUN was used to determine the amount of TS and its sulphur isotopic composition in each sediment sample.

Procedure: Sub samples of sediment were dried at 40°C or freeze-dried and ground in an agate mortar before dissolution in an HClO4-HNO3-HF acid mixture. The dried residue was dissolved in 1 M HCl for total sulphur (TS) analysis.

Approximately 15 mg of powdered sediment and >0.1 mg of V_2O_5 were accurately weighed into small tin cups using a Metler Toledo AT21 balance. The purpose of the V_2O_5 is to donate oxygen with a consistent $^{18}O/^{16}O$ ratio. The cups were gently compressed using tweezers to encapsulate the sample without any sample spillage and

folded into a small spherical shape for analysis of the total sulphur content and sulphur isotope composition ($^{34}S/^{32}S$ ratio) of organic matter by CF-IRMS as described by Böttcher et al. (1998). The sulphur and oxygen released during combustion combines to form SO_2 gas, which enters the ion source of the mass spectrometer through a split interface. In the mass spectrometer, integrated peaks for $^{32}SO_2^+$ and $^{34}SO_2^+$ are compared to the response for a standard gas sample. The $^{34}S/^{32}S$ ratio and $\delta^{34}S$ value are subsequently calculated.

All isotopic analyses during this study were run against internal MUN standards Canada Bay Marble (CBM) and the graphite standard USGS-24 for $\delta^{13}C$, and NZ-1 and NBS-123 for $\delta^{34}S$. Results are reported referenced to PDB for carbon ($\delta^{13}C$ = 0.75 VPDB (for CBM) and $\delta^{13}C$ = -16.00 VPDB for USGS-24) and are reported referenced to CDT for sulphur ($\delta^{34}S$ = -0.30 vs. CDT for NZ-1 and $\delta^{34}S$ = 17.09 vs. CDT for NBS-123) respectively. Absolute standard deviations in $\delta^{13}C_{org}$ and $\delta^{34}S$ analyses are below 0.20‰.

TOC and TS measurements were performed according to standard laboratory procedures and all procedures were checked with international and in-house standards. Relative standard deviations in duplicate measurements are lower than 1% for sulphur analyses, and lower than 5% for TOC duplicate measurements.

2.5.2.3 Biogenic opal (silica)

Biogenic opal or silica (BSi) concentration in sediment samples is generally quantified by measuring amorpbous silica as a fraction of total dry weight. The biogenic opal data presented in this study was determined based on the alkaline extraction method

of Mortlock and Froelich (1989). Selective chemical dissolution is used to remove opal from the sample and the silica concentration in the solution is measured by spectrometry. The biogenic silica was extracted and quantified with an extraction into sodium carbonate (Na_2CO_3) solution by Michelle Alexander at the Department of Earth Sciences, MUN.

Procedure: Samples were freeze-dried, powdered, weighed, and placed in 50 ml centrifuge tubes. The sample was then oxidized using 10% H_2O_2 solution to remove organic carbon and then decarbonated using 5 ml of 1 N HCl. 20 ml of deionized water was then added to each tube. The samples were then centrifuged at 4500 rpm, and the supernatant discarded. To a weighed 100 mg portion of the residual biogenic and terrigenous silica obtained after organic carbon removal and decarbonation, a single-step extraction of silica was performed on the samples by adding 100 ml of 2 M Na_2CO_3. The solution was then boiled at ca. 85°C for 5 hr to extract biogenic silica. After centrifugation, 20 ml of the supernatant was transferred to a polyethylene vial. Dissolved silica in the solution was subsequently determined by modified molybdate blue spectrophotometry where the silica is revealed by a molybdate complex and measured by spectrophotometry. Absorbances were read at 812 nm. In this study, the biogenic silica (opal) content are presented in % of dry weight of the non-organic and carbonate-free part of the sample as estimated from equation:

$$\text{Biogenic opal (\%)} \quad 2.4 \times \%\ SiO_{2opal} \qquad (1)$$

where SiO_{2opal} is the percentage of silica extracted into solution measured by spectrophotometry and the factor of 2.4 corrects for mineral contribution to the silica pool, which includes the average water content of diatomaceous silica (about 10% water $=SiO_2 \times 0.4\ H_2O$, Barcena et al., 2002).

CHAPTER THREE

3.0 Results

3.1 Chronological Data

Radiocarbon dates had been previously reported for four of the cores examined in this study (Aksu et al., 2002) as uncalibrated conventional ^{14}C dates in yr BP (half life of 5568 yr; errors represent 68.3% confidence limits). Corresponding calibrated calendar years have been determined using OxCal (Stuvier et al., 1998a,b) and a marine reservoir correction of 415 yr (Marine Reservoir Correction Database, Queens University, Belfast, Ireland). These calibrated ages supersede those published by Aksu et al. (2002) because some errors have been discovered in their reported calendar ages. The chronological data are given in Table 3.1.

There are no radiocarbon dates available for core MAR98-11; however, the lithostratigraphic correlation of this core to MAR98-12, from the same basin, permits approximate age assignments for MAR98-11.

Some basin wide depositional and environmental events can also be used to establish the approximate age in undated cores. For example, recent studies (e.g. Çağatay et al., 2000;Tolun et al., 2002) have shown that the late glacial to Holocene sediments of the Marmara Sea can be subdivided into an upper marine interval (Unit 1) and a lower lacustrine interval (Unit 2). The Unit 1/2 boundary has been dated to a ^{14}C age of ca. 1200 yr BP. Within Unit 1, two sapropelic layers are dated as 10500 – 6400 yr BP and 4750–3200 yr BP (Çağatay et al., 2000).

Core #	Depth (cm)	^{14}C date (yr BP)	Calendar Age (cal BP)
MAR00-5	60	5 460 ± 70	5 610 ± 210
MAR00-5	167	6 660 ± 60	6 875 ± 120
MAR00-6	45	2 160 ± 60	1 455 ± 60
MAR00-6	124	7 770 ± 70	7 0 ± 127
MAR00-8	54	5 780 ± 70	5 915 ± 160
MAR00-8	116	6 590 ± 70	6 810 ± 142
MAR98-12	50	4 200 ± 100	4 475 ± 230
MAR98-12	130	10 660 ± 130	10 705 ± 325

Table 3.1: Chronological Data for cores MAR00-5, MAR00-6, MAR00-8 and MAR98-12

3.2 Black Sea Cores

3.2.1 Core MAR00-5

3.2.1.1 TOC and carbon isotopic composition ($\delta^{13}C$)

In the Black Sea core MAR00-5, total organic carbon (TOC) contents range from 1.37% to 2.13% (Fig. 3.1; Table 3.2). TOC concentrations are relatively high in the upper 60 cm of the core gently fluctuating between 2.13 and 1.84%. There is a notable decrease in TOC to ~1.57% at 70 cm depth in the core. A progressive downcore increase is observed from 1.62 % at 80 cm to 2.13% at 130 cm; thereafter, a progressive downward decrease occurs in the remainder of the core with a minimum of 1.5% at 170 cm (Fig. 3.1; Table 3.2).

According to Kidd et al (1978), organic-rich layers that are >1cm thick and have ≥2% organic carbon are *sapropels*. Layers having similar thickness and 0.5-2% organic carbon are termed *sapropelic*. Following these definitions, and because sampling interval for this study is 10 cm, sapropels will only be recognized where two or more successive samples have TOC values ≥2%. Thus, most of the samples in core MAR00-5 are sapropelic muds. However, true sapropels with ≥2.0% TOC are observed at ~20-30 cm in this core.

The carbon isotopic composition of the total organic carbon $\delta^{13}C_{TOC}$ (hereafter referred to as $\delta^{13}C$) ranges from -24.34‰ to -26.24‰ in core MAR00-5 (Fig. 3.1; Table 3.2), slightly lighter than the reported value of -22‰ for modern plankton in the Black Sea (Deuser, 1970). From a $\delta^{13}C$ value of -25.52‰ at the core

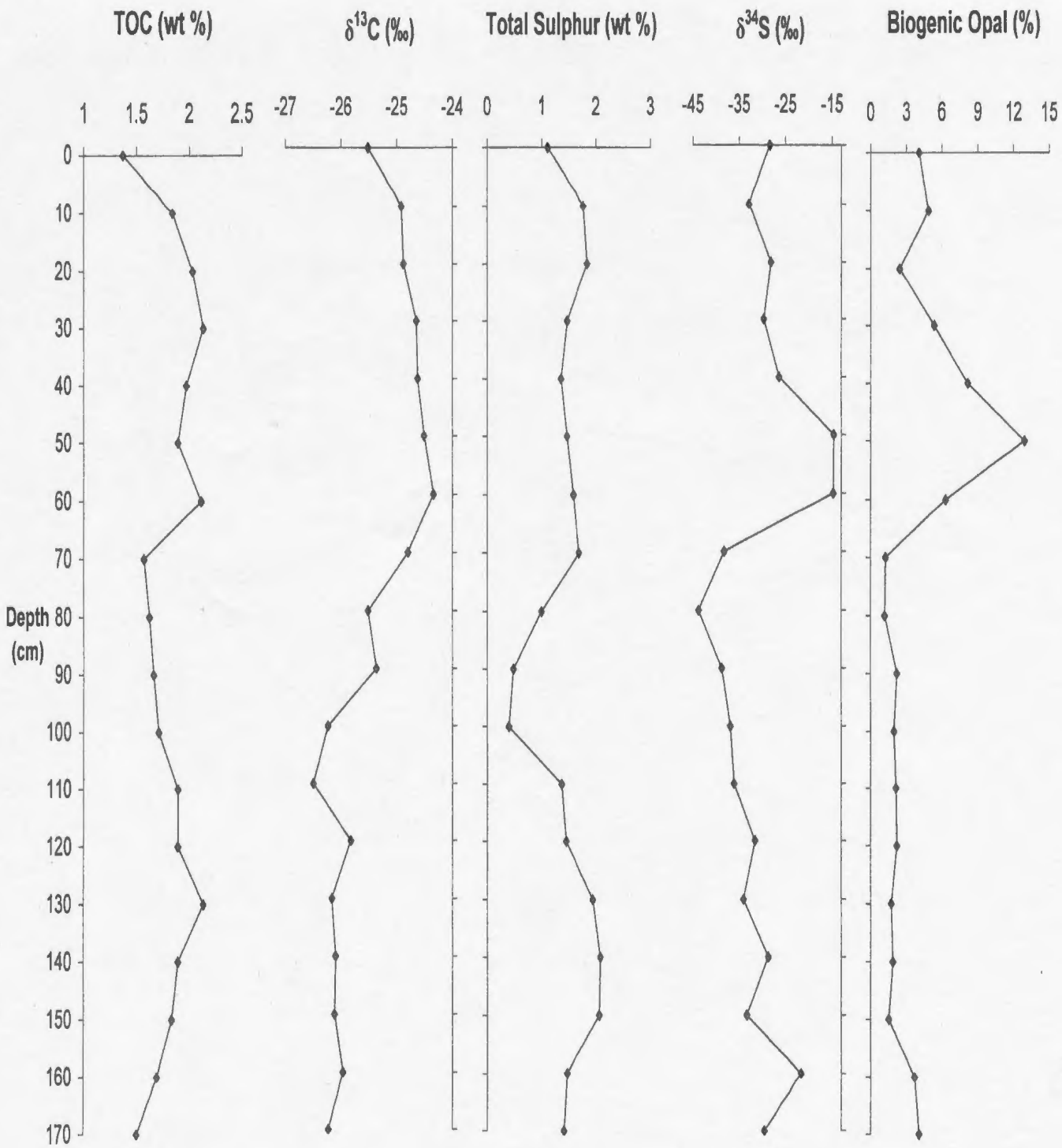


Fig. 3.1: Depth profiles of total organic carbon (TOC), carbon isotope composition ($\delta^{13}C$), total sulphur (TS), sulphur isotopic composition ($\delta^{34}S$) and biogenic opal (silica) for core MAR00-5.

Depth (cm)	TOC (wt %)	$\delta^{13}C$ (‰)	Sulphur (wt %)	$\delta^{34}S$ (‰)	Biogenic Opal (%)
0	1.37	-25.52	1.11	-28.41	4.06
10	1.84	-24.92	1.76	-32.92	4.86
20	2.03	-24.88	1.83	-28.16	2.44
30	2.13	-24.65	1.46	-29.71	5.35
40	1.97	-24.63	1.35	-26.45	8.16
50	1.89	-24.51	1.46	-14.65	12.92
60	2.11	-24.34	1.58	-14.74	6.31
70	1.57	-24.80	1.68	-38.25	1.25
80	1.62	-25.52	0.99	-43.82	1.20
90	1.66	-25.37	0.48	-38.76	2.24
100	1.71	-26.24	0.39	-36.95	1.96
110	1.89	-26.50	1.36	-36.14	2.15
120	1.89	-25.83	1.44	-31.61	2.21
130	2.13	-26.17	1.94	-34.11	1.75
140	1.89	-26.10	2.08	-28.77	1.88
150	1.83	-26.12	2.06	-33.37	1.54
160	1.69	-25.97	1.46	-21.68	3.70
170	1.50	-26.23	1.40	-29.60	4.07

Table 3.2: Analytical results of total organic carbon (TOC), carbon isotope composition ($\delta^{13}C$), total sulphur (TS), sulphur isotopic composition ($\delta^{34}S$) and biogenic opal (silica) for core MAR00-5. Sapropels with two or more successive values of TOC $\geq$2% are indicated in the shaded area.

top, there is a downcore trend towards progressively more positive $\delta^{13}C$ values in the upper 60 cm of the core, reaching a $\delta^{13}C$ value of -24.34‰ at 60 cm. A slight depletion to -24.8‰ was observed at 70 cm.

There is a rapid decrease to -25.52‰ at 80 cm, followed by depletion to the lowest $\delta^{13}C$ value of -26.50‰ in the core at 110 cm. A slight enrichment to a more positive $\delta^{13}C$ value (-25.83‰) is observed at 120 cm, just before the elevated TOC value at 130 cm. Thereafter, for the remainder of the core, $\delta^{13}C$ values fall in the narrow range from -26.5‰ to -26.23‰ (with an average of –26.09‰).

3.2.1.2 Total sulphur and sulphur isotopic composition ($\delta^{34}S$)

The total sulphur content in this core is generally high, with values ranging from 0.39-2.06 % (Fig. 3.1; Table 3.2). There is higher total sulphur in the upper part of the core with total sulphur concentration fluctuating between 1.11% at the top of the core to 1.68% at 70 cm. Below this depth, there is a rapid decrease in the next 30 cm to a minimum total sulphur value of 0.39% at 100 cm. Below 100 cm and for most of the remainder of the core, total sulphur increases to values like that at the core top. Distinct zones of elevated sulphur concentrations coincide with the sapropel (Fig. 3.1; Table 3.2).

Downcore sulphur isotope compositions ($\delta^{34}S$) in core MAR00-5 show an initial depletion from -28.4‰ at the core top to -32.92‰ at 10 cm (Fig. 3.1; Table 3.2). For the next 30 cm, there is an irregular pattern with values fluctuating between -28.16‰ to -26.45‰ at 40 cm.

A maximum value of $\delta^{34}S$ occurs at 50–60 cm depth that coincides with a distinct peak in TOC content. There is also a negative downward shift in $\delta^{34}S$ between 60 and 70 cm depth (from values of -14.74‰ to -38.25‰), culminating in a minimum $\delta^{34}S$ value of -43.82‰ at 80cm. Below this depth, there is a progressive enrichment towards positive $\delta^{34}S$ values downcore to -21.68‰ at 170 cm except for occasional fluctuations to lighter $\delta^{34}S$ values. $\delta^{34}S$ is -29.6‰ at the bottom of the core (Fig. 3.1; Table 3.2).

3.2.1.3 Biogenic opal (silica)

Biogenic opal values vary in an irregular fashion in core MAR00-5 (Fig. 3.1; Table 3.2). In the upper 50 cm of the core, there is a progressive increase in biogenic opal values from 4.06% at the core top to a maximum value of 12.92% at 50 cm, interrupted by a minimum of 2.44% at 20 cm, which marks the termination of sapropel deposition.

After the observed maximum at 50 cm, a sharp decrease occurs in the next 20 cm, which coincides with elevated TOC content (2.11%) at 60 cm depth. The lowest value of biogenic opal is 1.20% at 70 cm. Below 80 cm, biogenic silica values are nearly constant through the remainder of the core).

3.2.2 Core MAR00-6

3.2.2.1 TOC and carbon isotopic composition ($\delta^{13}C$)

TOC contents are relatively high in the Black Sea core MAR00-6 and range from 1.62 to 2.71% (Fig. 3.2; Table 3.3). Sediment samples in this core are sapropelic

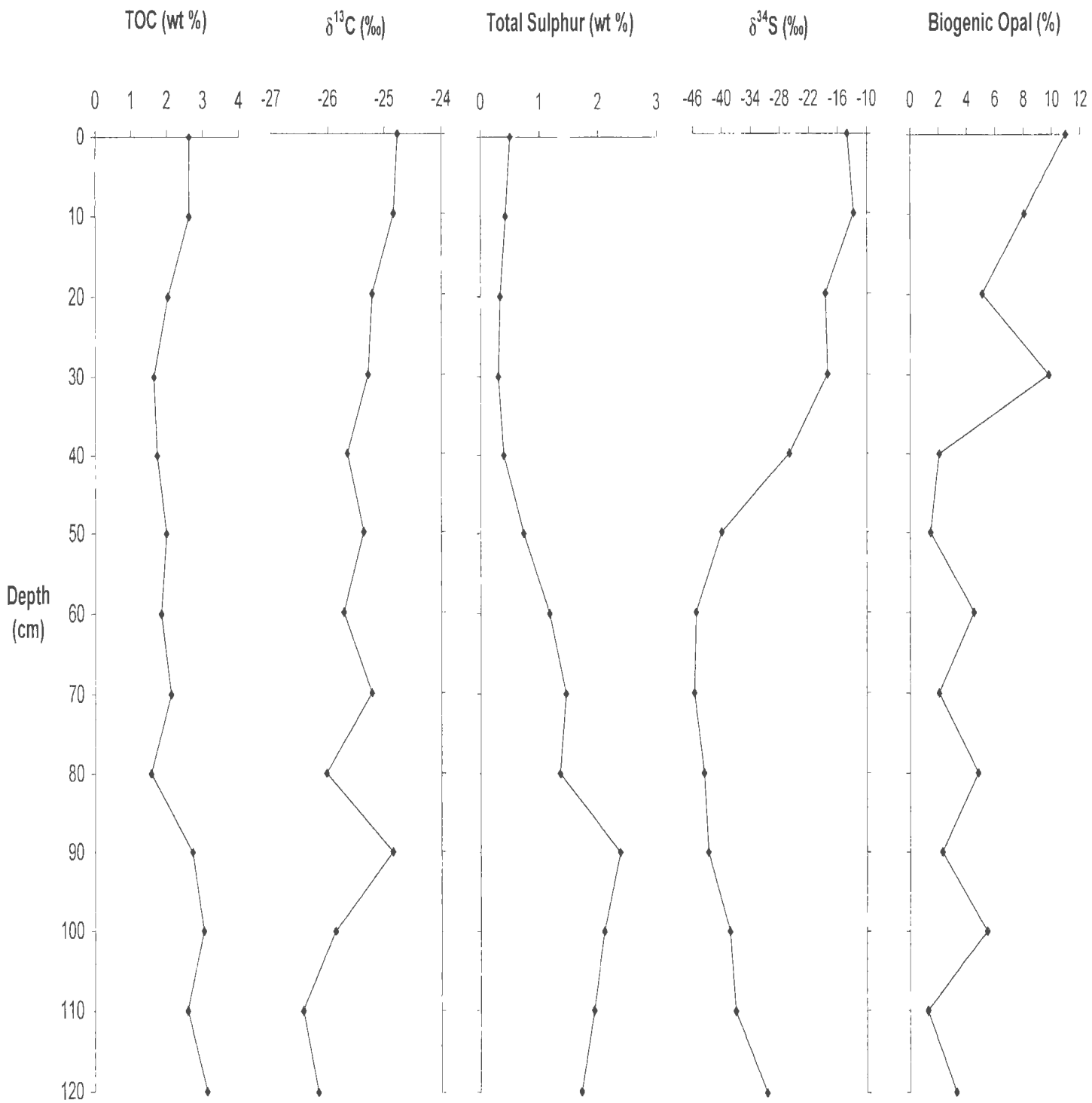


Fig. 3.2: Depth profiles of total organic carbon (TOC), carbon isotope composition ($\delta^{13}C$), total sulphur (TS), sulphur isotopic composition ($\delta^{34}S$) and biogenic opal (silica) for core MAR00-6.

Depth (cm)	TOC (wt %)	δ13C (‰)	Sulphur (wt %)	δ34S (‰)	Biogenic Opal (%)
0	2.62	-24.77	0.50	-14.08	10.96
10	2.62	-24.84	0.42	-12.70	8.06
20	2.03	-25.22	0.33	-18.56	5.09
30	1.64	-25.29	0.30	-18.13	9.79
40	1.73	-25.66	0.39	-25.99	2.05
50	1.98	-25.37	0.73	-40.06	1.45
60	1.84	-25.72	1.17	-45.39	4.52
70	2.11	-25.23	1.45	-45.77	2.05
80	1.56	-26.03	1.35	-43.71	4.82
90	2.71	-24.86	2.38	-42.85	2.26
100	3.02	-25.87	2.11	-38.37	5.44
110	2.58	-26.44	1.93	-37.19	1.25
120	3.12	-26.17	1.72	-30.66	3.26

Table 3.3: Analytical results of total organic carbon (TOC), carbon isotope composition ($\delta^{13}C$), total sulphur (TS), sulphur isotopic composition ($\delta^{34}S$) and biogenic opal (silica) for core MAR00-6. Sapropels with two or more successive values of TOC $\geq$2% are indicated in the shaded area.

muds with TOC values of 1.56-1.98% from 20-60 cm and at 80 cm depth. The uppermost 20 cm of the core exhibit relatively high TOC values >2.0%, while there is also elevated TOC content (2.71-3.12%) in the basal part of the core (from 90–120 cm) (Fig. 3.2; Table 3.3). These two intervals represent true sapropel layers with the former and latter being ~ 20 cm and ~ 40 cm thick respectively.

The carbon isotopic data in core MAR00-6 ranges from -24.77‰ to -26.44‰ (Fig. 3.2; Table 3.3). Progressive downcore depletion in ^{13}C characterizes the upper section of the core while the upper sapropel exhibits relatively high $\delta^{13}C$ values. The uppermost part of the sapropel at 90-120 cm also displays relatively high $\delta^{13}C$ values, but there is a noticeable sharp decrease to lighter $\delta^{13}C$ values in the lower portion of this sapropel, culminating in a $\delta^{13}C$ value of -26.17‰ at the base of the core (Fig. 3.2; Table 3.3).

3.2.2.2 Total sulphur and sulphur isotopic composition ($\delta^{34}S$)

Total sulphur concentrations are high in core MAR00-6, with total sulphur values ranging from 0.30-2.38% (Fig. 3.2; Table 3.3). Total sulphur values are nearly constant in the upper 30 cm interval with values fluctuating between 0.50% and 0.30%. Between 40 and 90 cm depth in the core, total sulphur shows an increase from 0.39% to a maximum of 2.38% at 90 cm after which there is another progressive decrease to the bottom of the core. Relatively elevated total sulphur concentrations at 70 cm and 90-120 cm coincide with sapropels (Fig. 3.2; Table 3.3), but the sapropel at the core top does not show such high total sulphur values.

The sulphur isotopic data for core MAR00-06 indicate relatively heavier $\delta^{34}S$ values of -12.07‰ to -18.13‰ in the upper 30 cm of the core (Fig. 3.2; Table 3.3). $\delta^{34}S$ values then decrease sharply downward in the lower and basal section of the core, with a minimum $\delta^{34}S$ value of -45.77‰ at 70 cm depth coinciding with a layer of increased TOC concentration. Below 70 cm, there is a minor progressive enrichment trend towards relatively heavier $\delta^{34}S$ values culminating in a nevertheless quite light $\delta^{34}S$ value (in absolute terms) of -30.66‰ at the base of the core (Fig. 3.2; Table 3.3).

3.2.2.3 Biogenic opal (silica)

In core MAR00-6, biogenic opal ranges from 1.45%-10.96% (Fig. 3.2; Table 3.3). Apart from a spike of 9.79% at 30 cm depth, there is gradual decrease downcore in the upper 50 cm from a high value of 10.96% at the core top to 1.45% at 50 cm depth. Below, biogenic silica fluctuates between ~2% and ~5% (Fig. 3.2; Table 3.3).

3.2.3 Core MAR00-8

3.2.3.1 TOC and carbon isotopic composition ($\delta^{13}C$)

In the Black Sea core MAR00-8, TOC contents are quite high, ranging from 1.79 (10 cm) to 3.06% (70 cm) (Fig. 3.3; Table 3.4). Most of the TOC concentrations in this core are well above 2.0% except for the upper 20 cm interval and the base of the core (120 cm depth), which have TOC just below 2.0%. The sapropel from 30-110 cm depth accounts for the greater part of the core and has TOC contents from 2.31% at the top to 2.73% at the base.

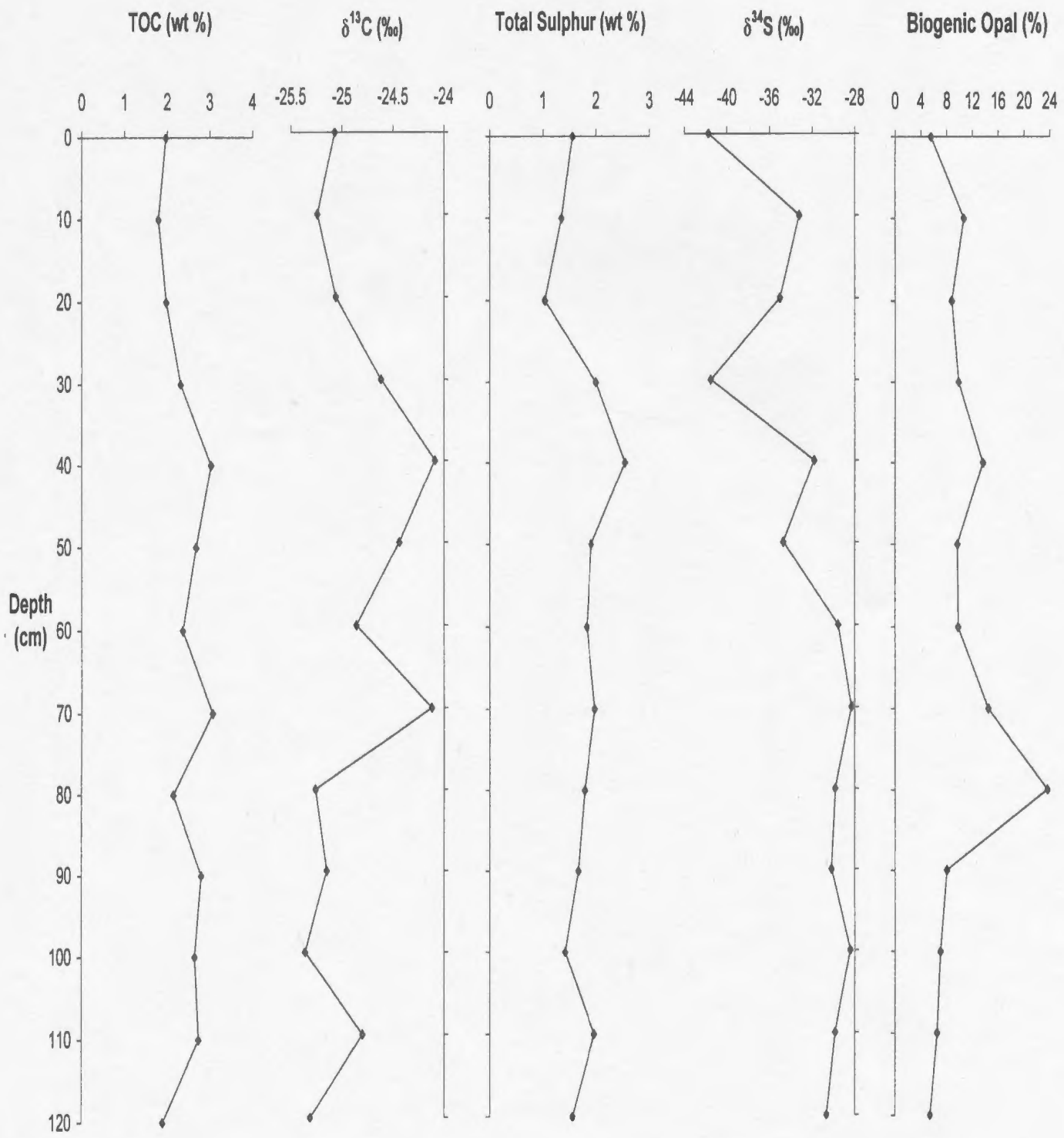


Fig. 3.3: Depth profiles of total organic carbon (TOC), carbon isotope composition ($\delta^{13}C$), total sulphur (TS), sulphur isotopic composition ($\delta^{34}S$) and biogenic opal (silica) for core MAR00-8.

Depth (cm)	TOC (wt %)	δ13C (‰)	Sulphur (wt %)	δ34S (‰)	Biogenic Opal (%)
0	1.96	-25.07	1.55	-41.75	5.54
10	1.79	-25.24	1.34	-33.23	10.69
20	1.97	-25.06	1.03	-35.03	8.79
30	2.31	-24.62	1.99	-41.52	9.87
40	3.02	-24.09	2.54	-31.81	13.67
50	2.67	-24.44	1.9	-34.72	9.73
60	2.36	-24.86	1.82	-29.56	9.82
70	3.06	-24.12	1.97	-28.32	14.52
80	2.14	-25.26	1.78	-29.84	23.70
90	2.79	-25.15	1.66	-30.18	8.08
100	2.64	-25.36	1.41	-28.42	7.05
110	2.73	-24.8	1.96	-29.85	6.55
120	1.89	-25.31	1.55	-30.66	5.45

Table 3.4: Analytical results of total organic carbon (TOC), carbon isotope composition ($\delta^{13}C$), total sulphur (TS), sulphur isotopic composition ($\delta^{34}S$) and biogenic opal (silica) for core MAR00-8. Sapropels with two or more successive values of TOC ≥2% are indicated in the shaded area.

$\delta^{13}C$ values in this core range from -24.09‰ to -25.36‰ (Fig. 3.3; Table 3.4). Downcore, there is a progressive enrichment in ^{13}C in the upper 40 cm. The substantial enrichment to 24.62‰ at 30 cm coincides with the top of the sapropel. With the exception of a relatively heavier $\delta^{13}C$ value at 70 cm, there is a decline of about 1‰ to lighter $\delta^{13}C$ values (average = -25.27‰) in the lower part to the core.

3.2.3.2 Total sulphur and sulphur isotopic composition ($\delta^{34}S$)

Total sulphur concentrations in core MAR00-8 are 1.41-2.54‰ (Fig. 3.3; Table 3.4). There is a progressive depletion in total sulphur values from the 0-20 cm section of the core below which there is an increase of about 1.51‰ over the next 20 cm. Thereafter, fluctuations between increases and decreases in total sulphur values occurs over the lower section of the core (Fig. 3.3; Table 3.4), with near-constant values below 50 cm. However the total sulphur values in this part of the core are generally higher than those close to the top of the core.

$\delta^{34}S$ values in core MAR00-8 range from -41.75‰ to -28.42‰ (Fig. 3.3; Table 3.4). There is an irregular enrichment from a light $\delta^{34}S$ value of -41.75‰ at the core top to a relatively heavier $\delta^{34}S$ value of -31.81‰ at 40 cm depth. A minimum $\delta^{34}S$ value of -41.52‰ at 30cm depth is coincident with the termination of sapropel deposition (Fig. 3.3; Table 3.3). From 60 cm downward, $\delta^{34}S$ values are relatively constant, heavy, and display minor fluctuations in the range -28.32‰ to -30.66‰ at the base of the core (Fig. 3.3; Table 3.4).

3.2.3.3 Biogenic opal (silica)

Biogenic opal values in core MAR00-8 are generally high, from 5.45-23.70% (Fig. 3.3; Table 3.3). A general progressive increase occurs from the core top to 80 cm depth. There is an initial downward increase in the uppermost 40 cm of the core from 5.45-13.67%. Below 40 cm depth, there is first a decline to 9.73%, followed by a downward increase to the highest biogenic opal value in the core of 23.70% at 80 cm depth (Fig. 3.3; Table 3.4). Between 80 cm and 90 cm, there is a major decrease of ~16% to a biogenic opal value of 8.08% at 90 cm depth. Values then decrease slowly to 5.45% at the base of the core.

3.3 Marmara Sea Cores

3.3.1 Core MAR98-11

3.3.1.1 TOC and carbon isotopic composition ($\delta^{13}C$)

TOC concentrations in core MAR98-11 are in the range 1.09-2.77% (Fig. 3.4; Table 3.5). There is a slight trend towards decreasing TOC content downcore in the uppermost 40 cm from 1.25 to 1.05%. Below, TOC increases over an 80 cm interval to 1.92% at 110 cm depth, just above the top of a 50 cm-thick sapropel layer (≥2% TOC). TOC values in this sapropel layer are quite high (average TOC = 2.37%) and at the base of the layer show a trend towards decreasing TOC concentration downcore. TOC is 2.77% at the top of the sapropel and 2.15% at the base. The transition out of the base of the sapropel layer is characterized by a TOC value of 1.96% at 170 cm depth. TOC values remain reasonably constant between 180 cm and

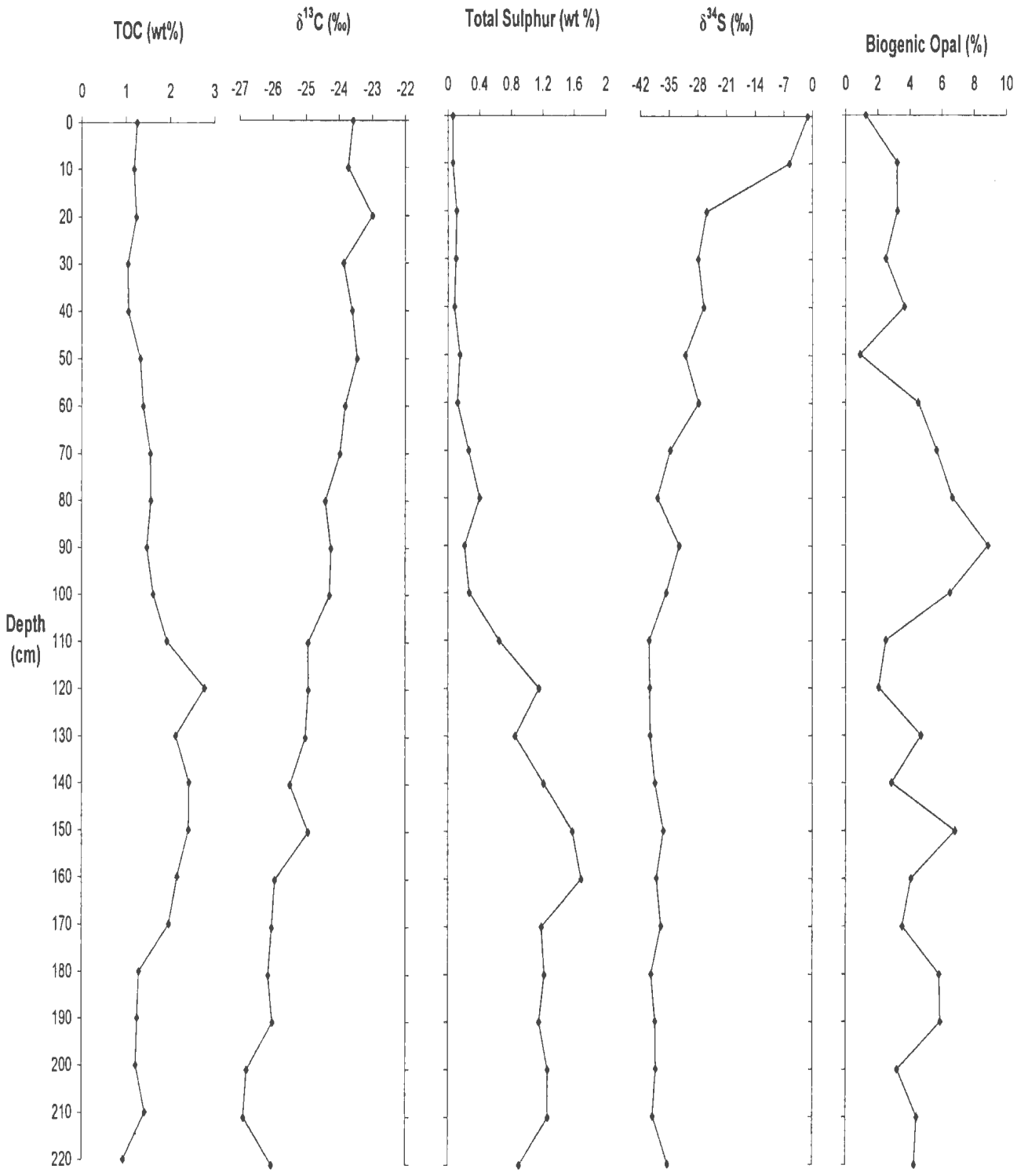


Fig. 3.4: Depth profiles of total organic carbon (TOC), carbon isotope composition ($\delta^{13}C$), total sulphur (TS), sulphur isotopic composition ($\delta^{34}S$) and biogenic opal (silica) for core MAR98-11.

Depth (cm)	TOC (wt %)	$\delta^{13}C$ (‰)	Sulphur (wt %)	$\delta^{34}S$ (‰)	Biogenic Opal (%)
0	1.25	-23.58	0.06	-1.19	1.25
10	1.18	-23.73	0.06	-5.63	3.19
20	1.23	-22.99	0.11	-25.87	3.21
30	1.04	-23.87	0.10	-27.91	2.50
40	1.05	-23.61	0.08	-26.55	3.65
50	1.32	-23.46	0.15	-31.03	0.89
60	1.39	-23.82	0.12	-27.77	4.50
70	1.55	-23.98	0.26	-34.73	5.65
80	1.56	-24.42	0.40	-37.84	6.64
90	1.47	-24.25	0.21	-32.51	8.86
100	1.61	-24.29	0.27	-35.70	6.50
110	1.92	-24.94	0.65	-39.87	2.51
120	2.77	-24.93	1.15	-39.72	2.06
130	2.12	-25.02	0.85	-39.62	4.69
140	2.42	-25.49	1.21	-38.45	2.85
150	2.41	-24.94	1.58	-36.37	6.81
160	2.15	-25.95	1.69	-38.07	4.07
170	1.96	-26.04	1.18	-37.02	3.51
180	1.29	-26.15	1.22	-39.4	5.82
190	1.25	-26.02	1.15	-38.43	5.90
200	1.22	-26.8	1.26	-38.28	3.19
210	1.42	-26.9	1.26	-39.02	4.41
220	0.93	-26.05	0.90	-35.42	4.27

Table 3.5: Analytical results of total organic carbon (TOC), carbon isotope composition ($\delta^{13}C$), total sulphur (TS), sulphur isotopic composition ($\delta^{34}S$) and biogenic opal (silica) for core MAR98-11. Sapropels with two or more successive values of TOC $\geq$2% are indicated in the shaded area.

the bottom of the core (Fig. 3.4; Table 3.5).

$\delta^{13}C$ values in core MAR98-11 range from -22.99‰ to -26.90‰ and display a notable progressive downcore depletion (i.e. more negative $\delta^{13}C$ with depth) from -23.5‰ at the core top to ~26.9‰ at the base. In the sapropel layer (120-160 cm depth), this trend towards depleted (i.e. lighter) $\delta^{13}C$ values is maintained with values fluctuating between -24.93 and –25.95‰ at the top and bottom of the sapropel, respectively.

3.3.1.2 Total sulphur and sulphur isotopic composition

Total sulphur content in core MAR98-11 ranges from 0.06% to 1.69% (Figure 3.4;Table 3.4). Total sulphur values in sediments from the upper 60 cm are generally low, ranging from 0.6% to 0.12%. Thereafter, total sulphur concentrations show a downcore increase with a minor peak of 0.4% at 80 cm depth and then a major increase below 100 cm depth. The highest value, (1.69%) in the core is at 160 cm depth (Fig. 3.4; Table 3.5). Intervals of relatively high sulphur enrichment (with total sulphur values ranging between 1.15-1.69%) are present 120 cm and 160 cm depth, which coincides with significantly higher TOC concentrations (i.e. the sapropel layer). However, total sulphur values remain relatively high below the sapropel (i.e. from 180 cm to the base of the core).

Apart from anomalously heavy $\delta^{34}S$ values of –1.19 and –5.63‰ at the top of the core, sulphur isotopic composition in core MAR98-11 is characterized by $\delta^{34}S$ values ranging from -25.87‰ to -39.02‰ (Fig. 3.4; Table 3.5). The $\delta^{34}S$ values

fluctuate between −25‰ and −31‰ from 20-60 cm depth, decrease irregularly to almost -40‰ by 110 cm, and then remain constant in the range -38‰ to -39‰ in the lower part of the core (Fig. 3.4; Table 3.5). The 110-160 cm depth (which is the sapropel layer) records the lowest (i.e. lightest) $\delta^{34}S$ values in the core with depletion to as much as −39.87‰. This depletion persists below the sapropel.

3.3.1.3 Biogenic opal (silica)

In core MAR98-11, biogenic opal values are relatively low to moderate and range from 0.89 to 8.86% (Fig. 3.4; Table 3.4). There is a gradual increase from a low of 1.25% at the core top to 3.65% in the upper 40 cm of the core. There is then a sharp decrease to an anomalously low biogenic opal value at 50 cm depth (0.89%), followed by an equally sharp increase in the next 10 cm to 4.50%. Below 60 cm, biogenic opal gradually increases to a maximum of 8.86% at 90 cm depth before dropping to 2.51% at the top of the sapropel at 110 cm depth.

The sapropel layer is characterized by relatively lower biogenic opal values fluctuating between 2.06% and 4.69%. Biogenic opal values fluctuate over a similar range, between 3.19% and 5.90% to the base of the core (Fig. 3.4; Table 3.5).

3.3.2 Core MAR98-12

The TOC, carbon isotopic composition and biogenic opal content reported for core MAR98-12 in this study were from the results from earlier extensive analysis of this core (e.g. Aksu et al., 2002; Hiscott and Aksu, 2002; Abrajano et al, 2002; Mudie

et al. 2002b; Kaminski et al. 2002). No total sulphur (TS) or sulphur isotopic data were available. These results are presented in Fig. 3.5 and Table 3.6 (see Aksu et al., 2002).

3.3.2.1 TOC and carbon isotope composition ($\delta^{13}C$)

In core MA98-12, TOC values are moderate to high in the upper 60 cm, ranging from 0.91 to ~1.6% with an overall increase downcore (Fig. 3.5; Table 3.6). A sharp increase to 2.08% at 30 cm marks the top of the ~40 cm thick sapropel which has TOC values fluctuating between 2.01% and 2.47%. From the base of the sapropel (100 cm), there is a progressive decrease in TOC concentrations downcore in the remaining part of the core. (Fig. 3.5; Table 3.6).

$\delta^{13}C$ values in core MAR98-12 range between –23.49‰ and -26.20‰. The biggest depletion in $\delta^{13}C$ is from 20-30 cm (-23.37—24.53‰). There is also depletion downcore in the sapropel (70-100 cm) with $\delta^{13}C$ values of -24.76‰ and -25.33‰ at the top and bottom of the sapropel layer, respectively. Below 100 cm, there is a sustained depletion trend downcore for the remaining 40 cm. The $\delta^{13}C$ values are fairly constant at -25.34‰ to -25.98‰ from 150 cm for the remainder of the core, with an average of -25.66‰ (Fig. 3.5; Table 3.6).

3.3.2.2 Biogenic opal (silica)

Biogenic opal (silica) values in core MAR98-12 are relatively high in Allo-subunit A1, ranging from 2.10% to 3.18% (Fig. 3.5; Table 3.6). Biogenic opal concentrations are notably lower in Allo-subunits A2 and Allounit B: 1.46-2.22% and

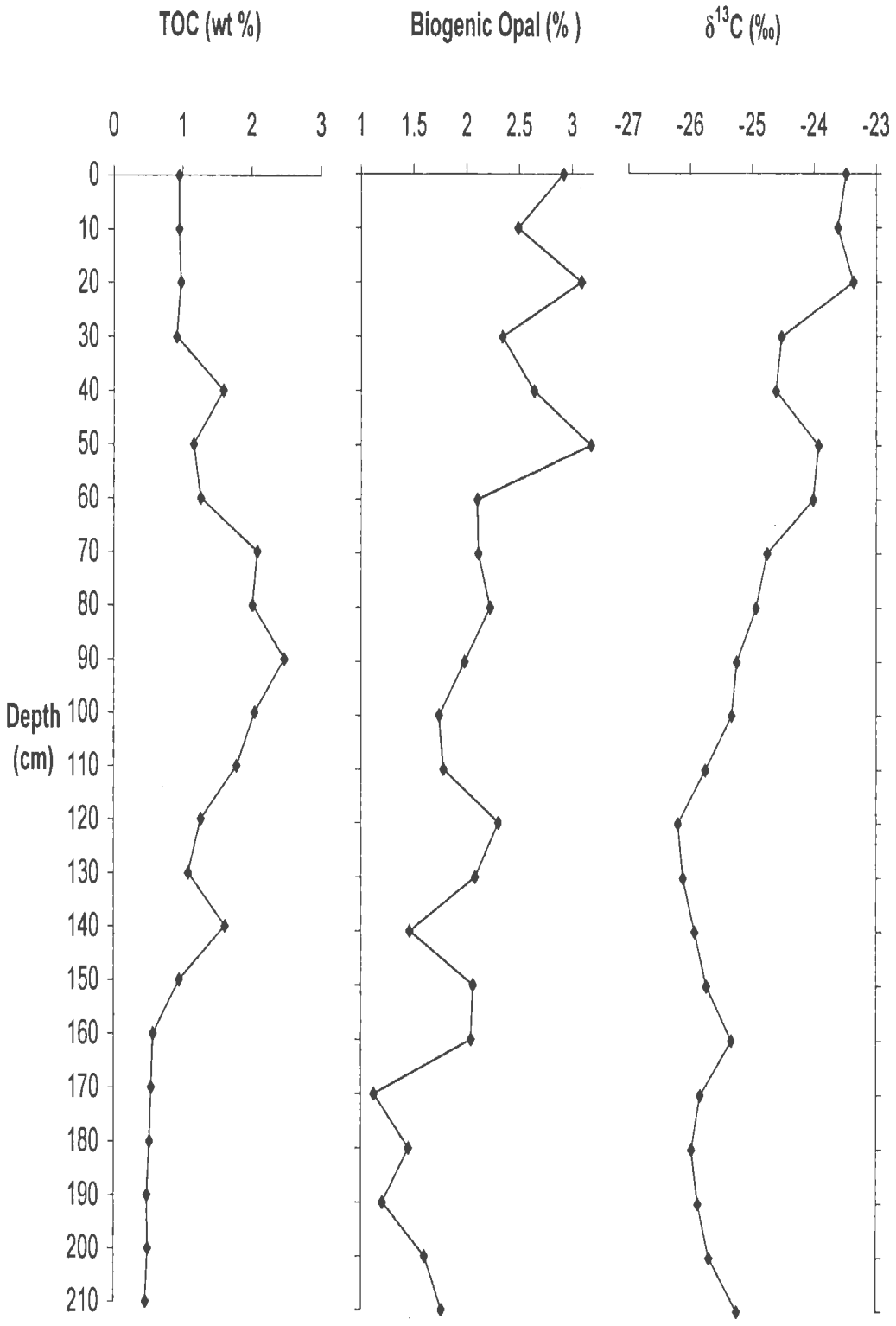


Fig. 3.5: Depth profiles of total organic carbon (TOC), carbon isotope composition ($\delta^{13}C$) and biogenic opal (silica) for Marmara Sea core MAR98-12.

Depth (cm)	TOC (wt %)	$\delta^{13}C$ (‰)	Biogenic Opal (%)	Allounit
0	0.95	-23.49	2.92	
10	0.95	-23.62	2.49	
20	0.97	-23.37	3.09	
30	0.91	-24.53	2.34	
40	1.59	-24.62	2.64	A1
50	1.16	-23.93	3.18	
60	1.26	-24.02	2.1	
70	2.08	-24.76	2.11	
80	2.01	-24.94	2.22	
90	2.47	-25.25	1.98	
100	2.04	-25.33	1.74	
110	1.78	-25.76	1.78	A2
120	1.26	-26.2	2.3	
130	1.08	-26.12	2.08	
140	1.61	-25.93	1.46	
150	0.95	-25.74	2.06	
160	0.57	-25.34	2.04	
170	0.54	-25.84	1.12	
180	0.52	-25.98	1.45	B
190	0.48	-25.88	1.2	
200	0.49	-25.7	1.6	
210	0.46	-25.25	1.76	

Table 3.6: Analytical results of total organic carbon (TOC), carbon isotopic composition ($\delta^{13}C$) and biogenic opal (silica) for core MAR98-12. Sapropels with two or more successive values of TOC $\geq$2% are indicated in the shaded area.

from 1.12–2.06%, respectively.

3.4 TOC-TS Trends

The relationship between carbon and sulphur contents (C/S ratio) shows changes, which are indicative of variations in the degree of salinity in the paleoenvironment (Berner, 1983;Berner and Raiswell, 1984). According to Berner and Raiswell (1984), C/S ratios <2 are generally considered representative of marine environments, whereas the C/S ratios >5 indicate relatively fresh water settings.

Sulphur and organic carbon relationships have also been used as an indicator of depositional environments (Leventhal, 1985) since the biogeochemical cycles of sulphur and carbon in sediments are coupled. In addition to data presented above for TOC, TS and their respective isotopic compositions, environmental conditions for the three Black Sea and one Marmara Sea (MAR98-11) core were also investigated using C/S ratios. Data for C/S ratios for the studied cores are given in Table 3.7 and plotted in Fig 3.6.

C/S ratios range from 0.91 to 4.32 in Black Sea core MAR00-5 (Table 3.7). In Black Sea core MAR00-6, C/S ratios are much higher than in core MAR00-5 with values fluctuating between 4.45 and 6.25 in the upper 40 cm, decreasing to 2.70 at 50 cm depth, followed by a trend towards decreasing values downcore culminating in a value of 1.81 at the base of the core. There are, however, particularly low ratios of ~1.15 at 80-90 cm depth. In Black Sea core MAR00-8, C/S ratios of 1.16 to 1.87 are comparable to those of MAR00-5 but are much lower than in the upper 50 cm of core

Depth (cm)	MAR00-5	MAR00-6	MAR00-8	MAR98-11
	C/S	C/S	C/S	C/S
0	1.24	5.27	1.46	20.83
10	1.04	6.25	1.74	19.67
20	1.11	4.97	0.99	11.18
30	1.45	5.36	0.91	10.4
40	1.46	4.45	1.19	13.12
50	1.29	2.70	1.47	8.80
60	1.34	1.58	1.20	11.58
70	0.93	1.45	1.72	5.96
80	1.64	1.15	1.29	3.90
90	3.48	1.14	1.98	7.00
100	4.32	1.43	1.35	5.96
110	1.39	1.34	1.39	2.95
120	1.31	1.81	1.22	2.41
130	1.10			2.49
140	0.91			2.00
150	0.89			1.52
160	1.15			1.27
170	1.07			1.66
180				1.06
190				1.09
200				0.97
210				1.13
220				1.03

Table 3.7: Analytical results of depth profiles of C/S ratios for cores MAR00-5, MAR00-6, MAR00-8 and MAR98-11.

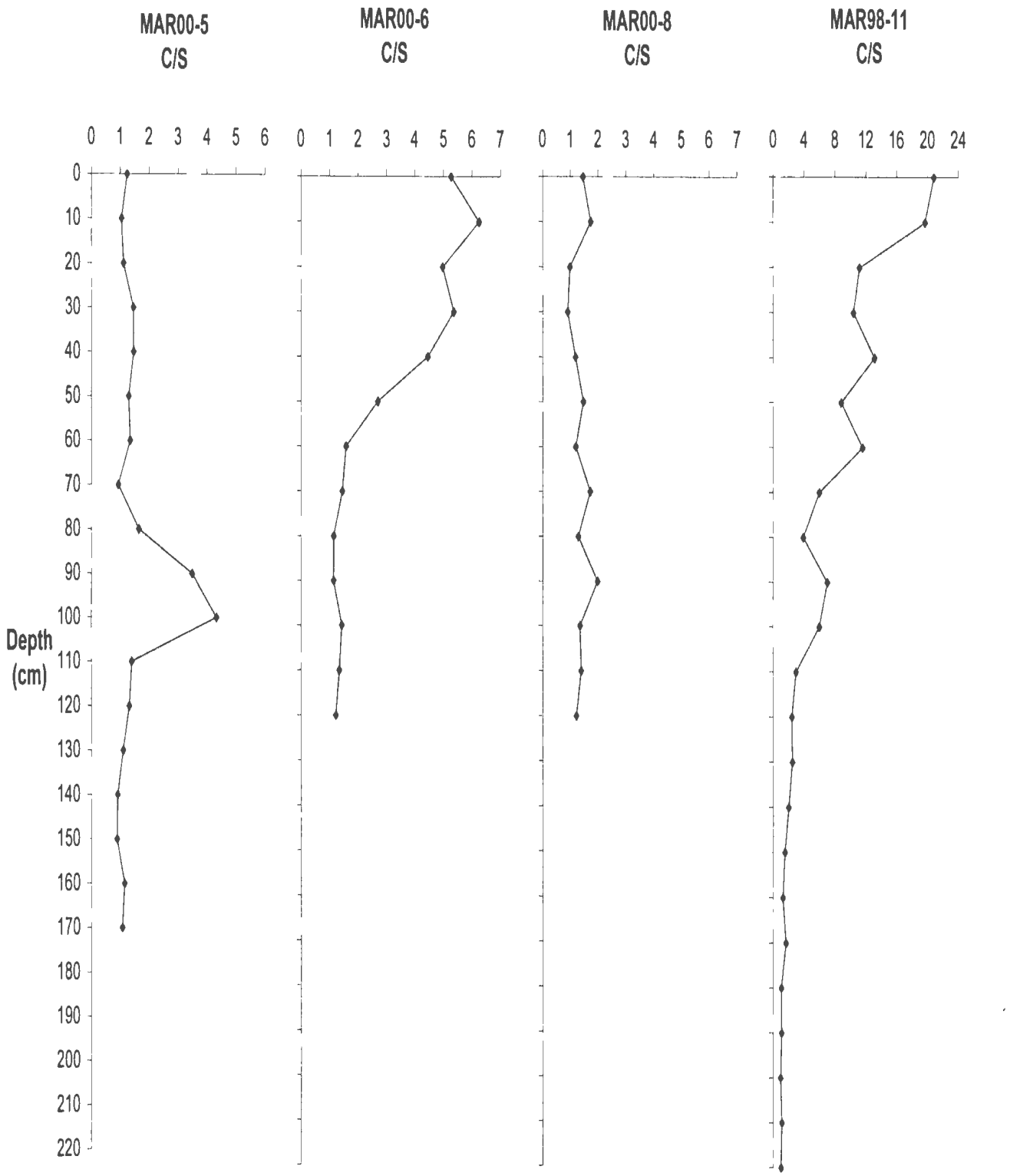


Fig. 3.6: Depth profile of C/S ratios for Black Sea cores MAR00-5, MAR00-6, MAR00-8 and Marmara Sea core MAR98-11.

MAR00-6 (Table 3.7).

In the Marmara Sea core MAR98-11, C/S ratios are extremely high with an initial value of 20.83 at the top of the core and a trend to relatively lower values downcore in the upper 70 cm interval (Table 3.7). There is a sharp decline to 5.96 at 70 cm depth after which there is a progressive decrease towards much lower values, a trend that continues to the base of the core where the C/S ratio is 1.03. The minimum value of 0.97 occurs at 200cm depth.

The implications of the ratios obtained in this study and the observed variation with depth for indications of depositional environments and for variations in the degree of salinity in the paleoenvironment of all the cores analyzed will be discussed in Chapter Four.

3.5 Quantitative Estimation of Organic Matter Sources

According to previous workers (Müller and Suess, 1979; Demaison and Moore, 1980; Arthur et al., 1984; Tissot and Welte, 1984; Emerson and Hedges, 1988; Stein, 1991; Calvert and Pedersen, 1992), the accumulation of marine and terrigenous organic carbon in marine environments is mainly a function of the rate of supply and the rate of preservation. According to Stein et al. (1989), changes in the accumulation of terrigenous organic matter in marine deposits mainly documents variations in terrigenous supply rather than changes in preservation. In contrast, changes in the accumulation of autochthonous organic matter under oxic water conditions, in most cases, document the combination of both processes (i.e., changes in paleoproductivity (supply) and diagenetic overprint (preservation)). This assertion is based on the fact that vascular plant matter reveals a higher resistivity to oxic

decomposition than marine organic matter and therefore, after surviving long distance transport to the marine environment, is selectively preserved in the sedimentary record (Tissot and Welte, 1984).

Thus, the detailed interpretation of sources and distribution of organic matter preserved in the sediment cores depends on the determination of the relative contributions of terrestrial and marine carbon to the total organic carbon (TOC). This quantitative approach has been widely combined with carbon isotopic data to provide information about variation in the source of organic matter, which in turn has implications for regional history of Quaternary changes in marine productivity and continental vegetation.

The $\delta^{13}C$ records of modern and Quaternary marine deposits have been commonly applied to evaluate the relative proportions of marine and terrigenous organic carbon to the TOC using the two-component mixing equation (Müller et al., 1983; Jasper and Gagosian, 1990; Stein, 1991; Westerhausen et al., 1993; Müller et al., 1994) given in equation (1).

$$\delta^{13}C_{sample} = F_{terr} \times \delta^{13}C_{terr} + F_{mar} \times \delta^{13}C_{mar} \quad (1)$$

where $\delta^{13}C_{sample}$ is the measured bulk carbon isotopic composition of the TOC, F_{mar} and F_{terr} are the contributions from marine and terrigenous sources, respectively and $\delta^{13}C_{mar}$ and $\delta^{13}C_{terr}$ indicate the carbon isotopic composition of marine and terrigenous organic matter, respectively. Assuming $F_{terr} + F_{terr} = 1$, Equation (1) can also be written as:

$$\delta^{13}C_{sample} = F_{terr} \times \delta^{13}C_{terr} + (1 - F_{terr}) \times \delta^{13}C_{mar} \quad (2)$$

Solving for F_{terr} in Equations (1) and (2), the mixing equation can be rearranged to estimate the relative contribution of terrestrially derived organic matter to the TOC in equation (3);

$$F_{terr} = \frac{(\delta^{13}C_{sample} - \delta^{13}C_{mar})}{(\delta^{13}C_{terr} - \delta^{13}C_{mar})} \quad (3)$$

where F_{terr} is the terrigenous fraction, $\delta^{13}C_{sample}$ is the measured bulk carbon isotopic composition of the sample, and $\delta^{13}C_{mar}$ and $\delta^{13}C_{terr}$ are the marine and terrestrial end members, respectively, from equation (1).

Application of this equation requires that we know, or can reasonably estimate, $\delta^{13}C_{mar}$ and $\delta^{13}C_{terr}$. For the Black and Marmara Seas, the end-member values used in the mixing equation were taken from stable carbon isotope values previously reported in literature; - 23‰ and -27‰ for $\delta^{13}C_{mar}$ and $\delta^{13}C_{terr}$ respectively (Aksu et al., 1999). The use of mixing equation (1) also assumes that there are no other sources; that there is no significant preferential loss or gain of the contribution from one source over another prior to deposition of the organic matter and that there is negligible carbon isotopic fractionation due to variations in temperature (Fontugne and Duplessy, 1978), changes in phytoplankton species (Fontugne, 1983), and variations in dissolved inorganic carbon concentrations in the basin (Rau et al., 1989).

Estimates of the relative contribution (in %) of terrigenous organic carbon to the TOC decrease upcore in both MAR00-6 and MAR98-11 (Table 3.8 and Fig. 3.7). In the upper 30 cm (upper sapropel) of core MAR00-6, the terrestrial and marine organic carbon fractions are roughly equal, while the lower sapropel from 100 cm depth to the base of core has a much higher relative contribution of terrigenous organic carbon. In core MAR00-5, there is a similar upcore decrease in F_{terr} from the base of the core to 50 cm depth, above which there is a progressive increase to the top of the core. In core MAR00-8, F_{terr} shows irregular

Depth (cm)	Terrigenous Fraction (%)			
	MAR00-5	MAR00-6	MAR00-8	MAR98-11
0	63	**44**	52	15
10	**48**	**46**	56	18
20	**47**	**56**	52	0
30	41	**57**	41	22
40	41	67	**27**	15
50	38	59	**36**	12
60	34	68	**47**	21
70	45	56	**28**	25
80	63	76	**57**	36
90	59	47	**54**	31
100	81	**72**	**59**	32
110	88	**86**	**45**	49
120	71	**79**	**58**	**48**
130	79			**51**
140	78			**62**
150	78			**49**
160	74			**74**
170	81			76
180				79
190				76
200				95
210				98
220				76

Table 3.8: Relative contribution of terrigenous organic carbon in % to the TOC in cores MAR00-5, MAR00-6, MAR00-8 and MAR98-11. Sapropels with two or more successive values of TOC ≥2% are indicated in bold. The terrigeneous fraction is calculated using equation (3) and assumed values of - 23‰ and -27 ‰ for $\delta^{13}C_{mar}$ and $\delta^{13}C_{terr}$ respectively

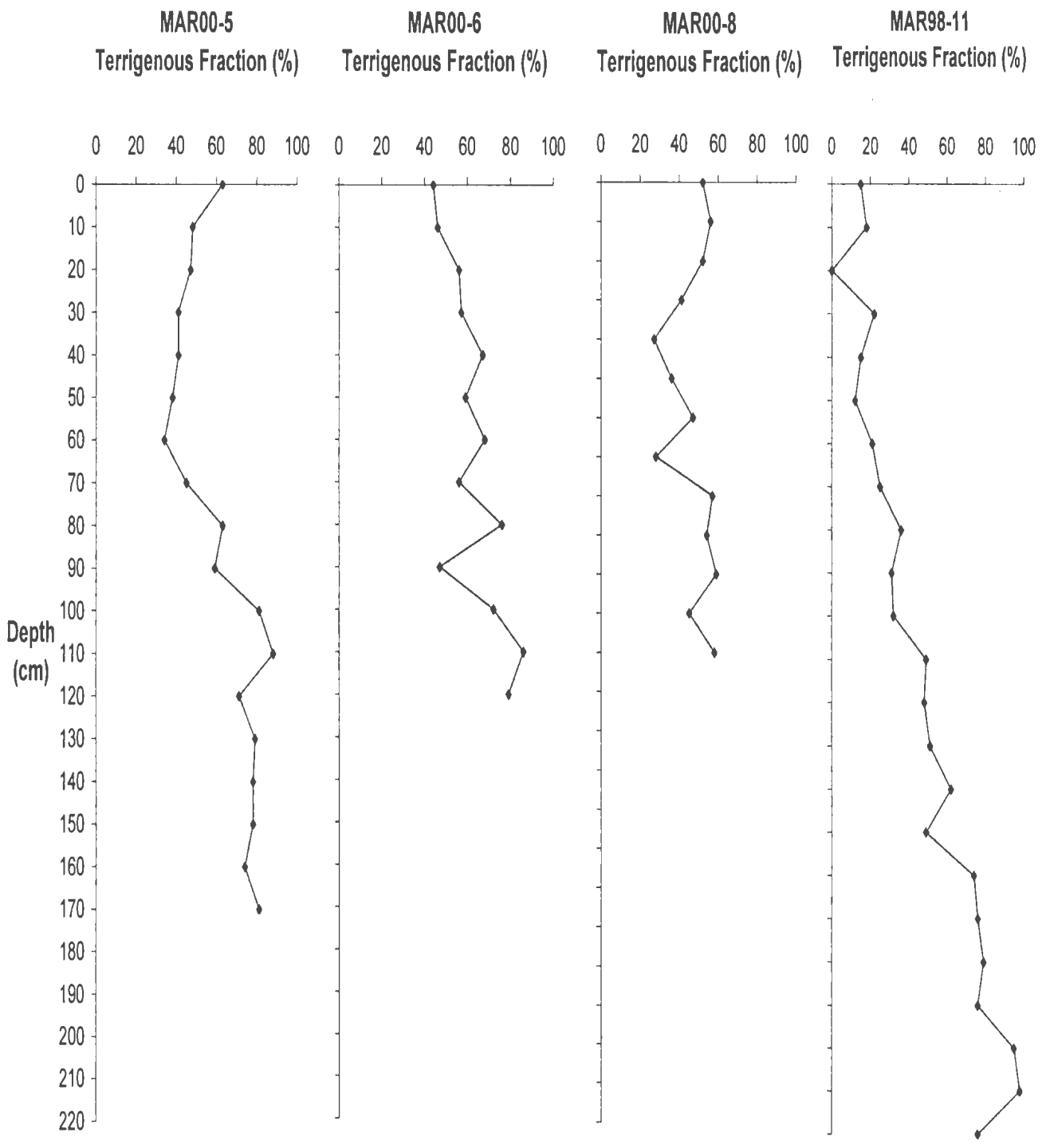


Fig. 3.7: Depth profile of the relative contribution of terrigenous sources (in %) to the TOC in cores MAR00-5, MAR00-6, MAR00-8 and MAR98-11.

fluctuations.

3.6 Sulphate Reduction and Organic Matter Degradation and Preservation

Anaerobic microbial reduction of sulphate to sulphide is primarily responsible for the degradation of organic matter in marine sediments (Jorgensen, 1982). This process is responsible for the oxidation of buried organic matter, which becomes relatively more important with increasing water depth and decreasing oxygen availability. Fisher and Hudson (1987) suggested that two moles of organic carbon are consumed to produce one mole of reduced sulphur during sulphate reduction, according to the equation:

$$SO_4^{2-} + 2CH_2O \Longrightarrow 2HCO^{3-} + H_2S \qquad (3)$$

Thus, quantification of organic matter oxidation by sulphate reduction can be achieved by measuring the concentration of a product of the sulphate reduction process: sedimentary sulphide, principally as pyrite (Imbus et al., 1992). This is usually achieved by measuring the total sulphur contents because total sulphur typically reflects the quantity of reduced sulphur (principally pyrite) in sediments.

3.6.1 Quantification of Organic Matter Degradation and Preservation by Sulphate Reduction

In conjunction with the measured total organic carbon (TOC) content, the total sulphur content in sediments was used to quantify the loss of organic carbon due to microbial sulphate reduction (Littke et al., 1991; Vetö and Hetényi, 1991; Lallier-Vergés et al., 1993; Bertrand and Lallier-Vergés, 1993; Vetö et al, 1994). The premise for this is that the measured TOC value is the residual organic matter after diagenetic and microbial degradation of some but not all of the original organic carbon. According to the authors

listed above, this premise holds only in non-bioturbated sediments where the amount of H_2S that escapes during sulphate reduction is limited. Hence, they concluded that in many bioturbated sediments, the original TOC contents will be underestimated since bioturbation generally results in a substantial loss of H_2S. To address this problem, the original percentages of organic carbon before the onset of sulphate reduction (TOC_{OR}), were subsequently calculated by Vetö et al. (1995) based on mass balance considerations and on stoichiometry for the bacterial sulphate reduction reaction using the following equation:

$$TOC_{OR} = TOC + TOC_{SR} \quad (4)$$

where TOC is the measured total organic carbon value. TOC_{SR} is the amount of organic carbon lost during sulphate reduction, calculated as follows:

$$TOC_{SR} = TS \times 0.75 \times 1.33 \quad (5)$$

where TS is the total sulphur content of the sediments. Stoichiometry of the sulphate reduction equation (3) shows that 1% of reduced sulphur in sediments corresponds to a 0.75% loss of TOC (Vetö et al., 1995), based on the atomic weights of carbon and sulphur and Equation 3. The value 1.33 in Equation 5 accounts for a 25% (diffusional) loss of reduced sulphur (mainly hydrogen sulphide), which occurs before it is converted to iron sulphide or other immobile sulphur species (Vetö et al., 1994). The ratio of the measured TOC to the original total organic carbon (TOC/TOC_{OR}) was then used as an indication of the degree of organic carbon preservation.

The results of the estimated original organic carbon content (TOC_{OR}) for all cores are presented in Table 3.9 and Figure 3.8. The TOC/TOC_{OR} ratio is presented in Table 3.10 and is plotted against depth in Figure 3.9 for all cores. These plots permit assessment of the

Depth (cm)	Core MAR00-5		Core MAR00-6		Core MAR00-8		Core MAR98-11	
	TOC_{SR} (%)	TOC_{OR} (%)	TOC_{SR} (%)	TOC_{OR} (%)	TOC_{SR} (%)	TOC_{OR} (%)	TOC_{SR} (%)	TOC_{OR} (%)
0	1.11	2.48	0.50	3.12	1.55	3.51	0.06	1.31
10	1.76	3.6	0.42	3.04	1.34	3.13	0.06	1.24
20	1.82	3.85	0.33	2.36	1.03	3.00	0.11	1.34
30	1.46	3.59	0.30	1.94	1.99	4.30	0.10	1.14
40	1.35	3.32	0.39	2.12	2.53	5.55	0.08	1.13
50	1.46	3.35	0.73	2.71	1.90	4.57	0.15	1.47
60	1.58	3.69	1.17	3.01	1.82	4.18	0.12	1.51
70	1.68	3.25	1.45	3.56	1.97	5.03	0.26	1.81
80	0.99	2.61	1.35	2.91	1.78	3.92	0.40	1.96
90	0.48	2.14	2.37	5.08	1.66	4.45	0.21	1.68
100	0.39	3.10	2.10	5.12	1.41	4.05	0.27	1.88
110	1.36	3.25	1.93	4.51	1.96	4.69	0.65	2.57
120	1.44	3.33	1.72	4.84	1.55	3.44	1.15	3.92
130	1.93	4.06					0.85	2.97
140	2.07	3.96					1.21	3.63
150	2.05	3.88					1.58	3.99
160	1.46	3.15					1.69	3.84
170	1.40	2.90					1.18	3.14
180							1.22	2.51
190							1.15	2.40
200							1.26	2.48
210							1.26	2.68
220							0.90	1.83

Table 3.9: Calculated original organic carbon (TOC_{OR}) and the loss of organic carbon by sulphate reduction (TOC_{SR}) values for cores MAR00-5, MAR00-6, MAR00-8 and MAR98-11.

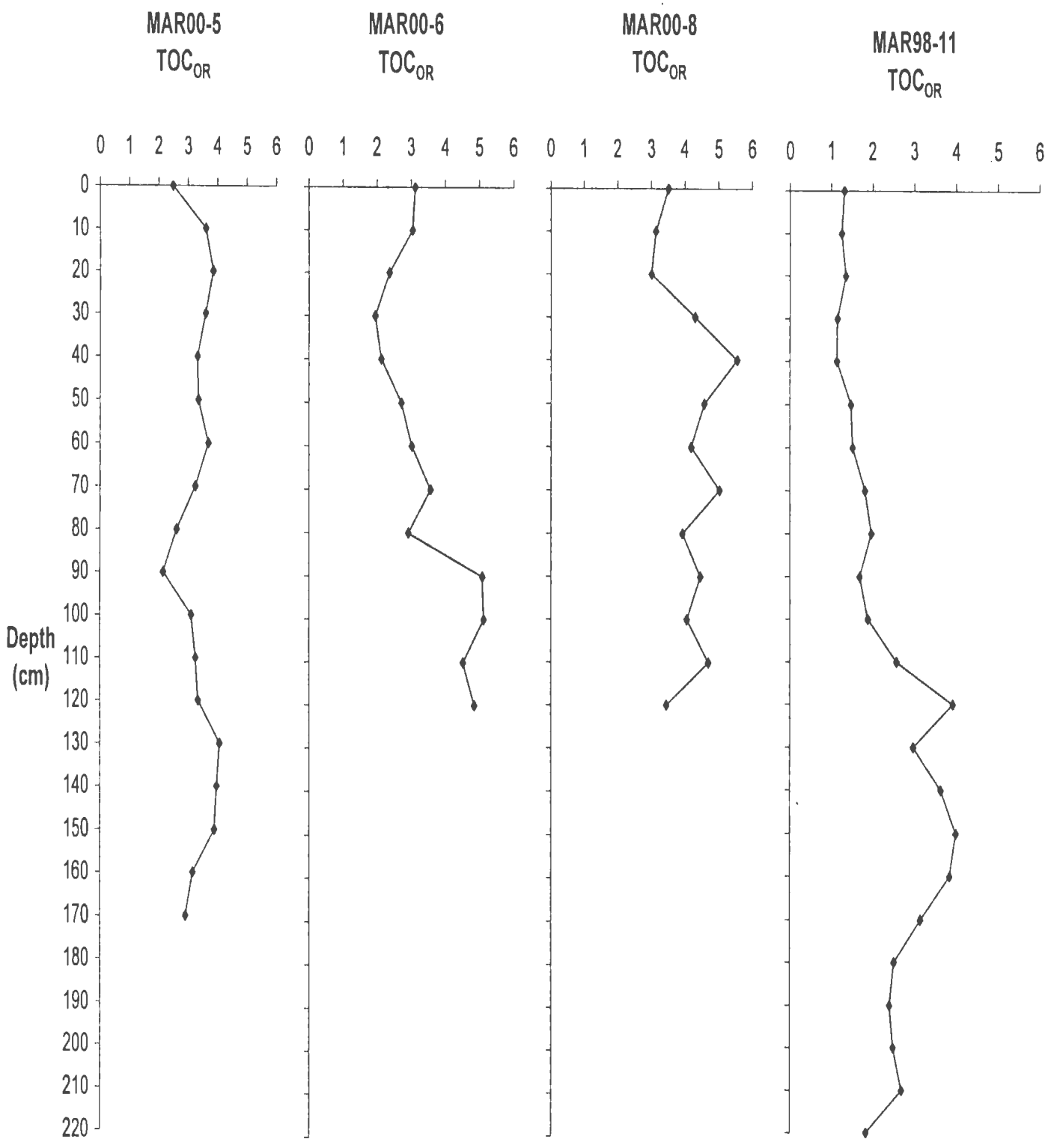


Figure 3.8: Depth profiles of calculated original organic carbon values (TOC_{OR}) for cores MAR00-5, MAR00-6, MAR00-8 and MAR98-11

Depth (cm)	TOC/TOC_{OR}			
	Core MAR00-5	Core MAR00-6	Core MAR00-8	Core MAR98-11
0	0.55	0.84	0.56	0.95
10	0.51	0.86	0.57	0.95
20	0.53	0.86	0.6	0.92
30	0.59	0.85	0.54	0.91
40	0.59	0.82	0.54	0.93
50	0.56	0.73	0.58	0.90
60	0.57	0.61	0.57	0.92
70	0.48	0.59	0.61	0.86
80	0.62	0.54	0.55	0.80
90	0.78	0.53	0.63	0.88
100	0.55	0.59	0.65	0.86
110	0.58	0.57	0.58	0.75
120	0.57	0.65	0.55	0.71
130	0.52			0.71
140	0.48			0.67
150	0.47			0.60
160	0.54			0.56
170	0.52			0.62
180				0.51
190				0.52
200				0.49
210				0.53
220				0.51

Table 3.10: TOC/TOC_{OR} ratio (degree of organic matter preservation) for cores MAR00-5, MAR00-6, MAR00-8 and MAR98-11.

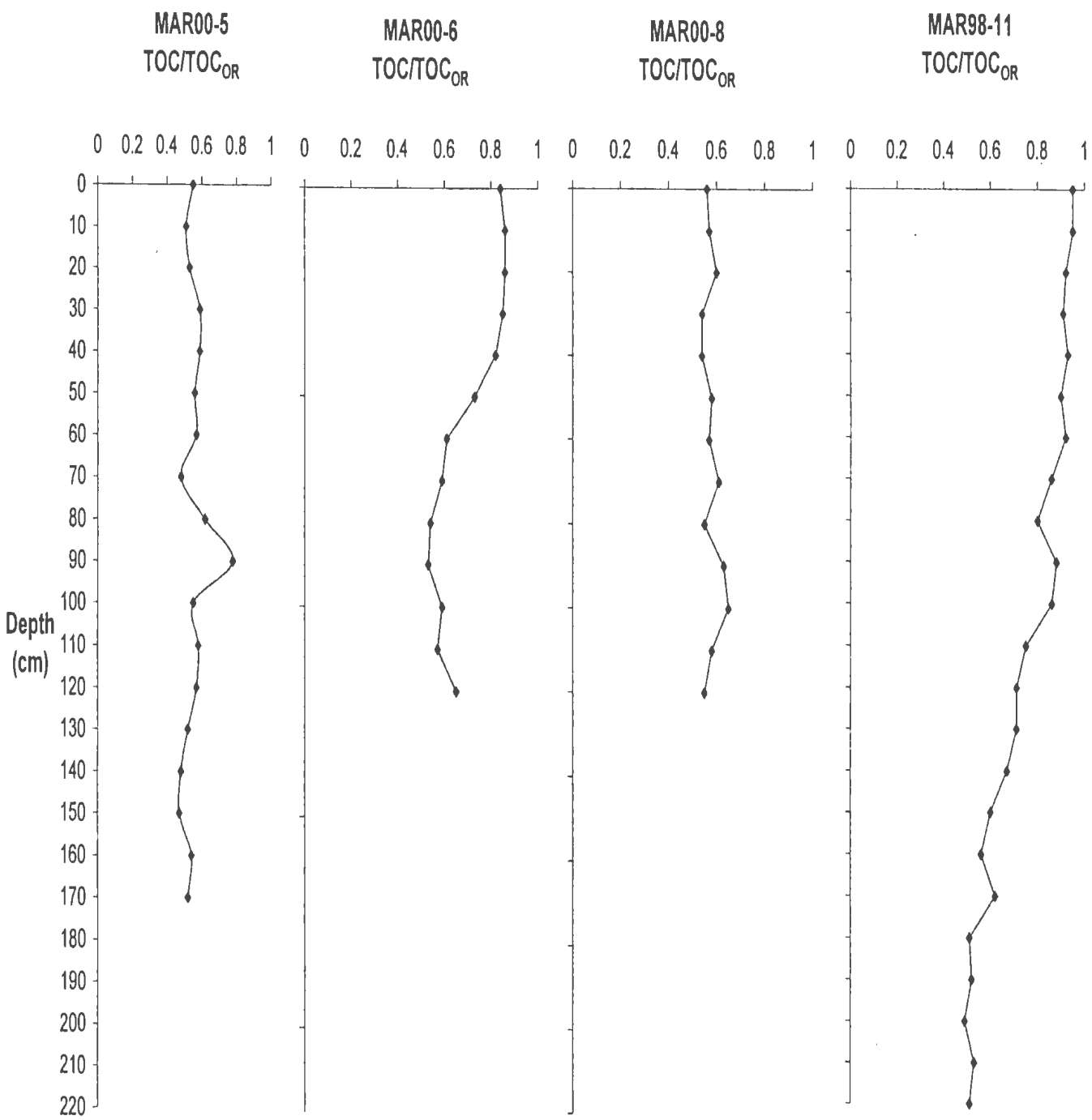


Figure 3.9: Depth profiles of the TOC/TOC$_{OR}$ ratio (degree of OM preservation) for cores MAR00-5, MAR00-6, MAR00-8 and MAR98-11

effect of the sulphate reduction process on the preservation of organic matter in sediments and generally treats any loss of hydrogen sulphide that may have occurred due to bioturbation as minimal. Interpretation of these plots is deferred to Chapter Four.

3.7 Age Control and Correlation of Marmara Sea Cores MAR98-12 and MAR98-11

To reconstruct a detailed history of environmental conditions that prevailed during the deposition of the sediments, it is necessary to establish a coherent stratigraphic framework with correct age assignments for the cores. Although no radiocarbon dating was done on core MAR98-11, visual core description revealed strong similarity in important lithological features such as structure, color and visible laminations with core MAR98-12. Both these cores were collected from deep nearby basins in the Marmara Sea. Thus, lithostratigraphic correlations with core MAR98-12 can be used to provide tentative ages for core MAR98-11.

This assumes that the development of large scale lithostratigraphic units and sapropel deposition are time synchronous in the Marmara Sea, and that the chronostratigraphic history of core MAR98-12 is well constrained from previous studies (e.g. Aksu et al, 1999, 2002 a, b).

3.7.1 Marker Event: Sapropel Deposition

Sapropels are common in eastern Mediterranean sediments and always occur at the same stratigraphic levels, so are considered to be synchronous events. Sapropels in the eastern Mediterranean have been extensively dated and provide a high

chronostratigraphic precision over the last few million years, which allows a detailed and accurate comparison of identical time intervals in the sedimentary record of different cores.

Although Kidd et al. (1978) defined *sapropels* as layers that are >1cm thick and have ≥2% organic carbon, the recognition of sapropels in the literature has deviated from these guidelines, particularly the absolute TOC value. In fact, several sapropel assignments have been made on ≥1.5% TOC content (e.g. Çağatay et al., 2000) and on the basis of lithological characteristics such as color or structure, without reference to organic carbon content (Murat and Got, 2000). In this study, a combination of both lithologic features as well as the definition given by Kidd et al. (1978) will be used to recognize sapropels.

In the Marmara Sea, two sapropel layers have been previously identified. Çağatay et al. (2000), Aksu et al. (2002) and Abrajano et al. (2002) have reported that sapropels M2 and M1 were deposited between ~29.5 and 23.5 ka, and ~10.5 and 6.0 ka, respectively. They used color changes and ≥1.5% TOC content, and not strict adherence to the definition of Kidd et al. (1978). Thus, using sapropel characteristics in the undated core MAR98-11 and its correlation with comparable sapropel in the dated core MAR98-12, important boundaries in core MAR98-11 can be approximately dated. A summary of similar lithologic features (by depth intervals) in both cores is given in Table 3.11. In particular, laminated darker muds that were described as sapropel can be correlated between the two cores. (Figure 3.10, Table 3.11)

In core MAR98-11, the sapropel that is contemporaneous to the sapropel in core MAR98-12 (67-130 cm) has been recognized from 108-180cm, based on color changes. In both cores, the upper part is significantly bioturbated, contains abundant iron monosulphide

Lithologic feature	Core MAR98-12	Core MAR98-11
Sapropel	67–143 cm	108–185 cm
TOC ≥ 2%	70–100 cm	120 –160 cm
Laminated Interval	100–143 cm	147–185 cm

Table 3.11: Summary of similar lithologic features (by depth intervals) in core MAR98-11 and core MAR98-12.

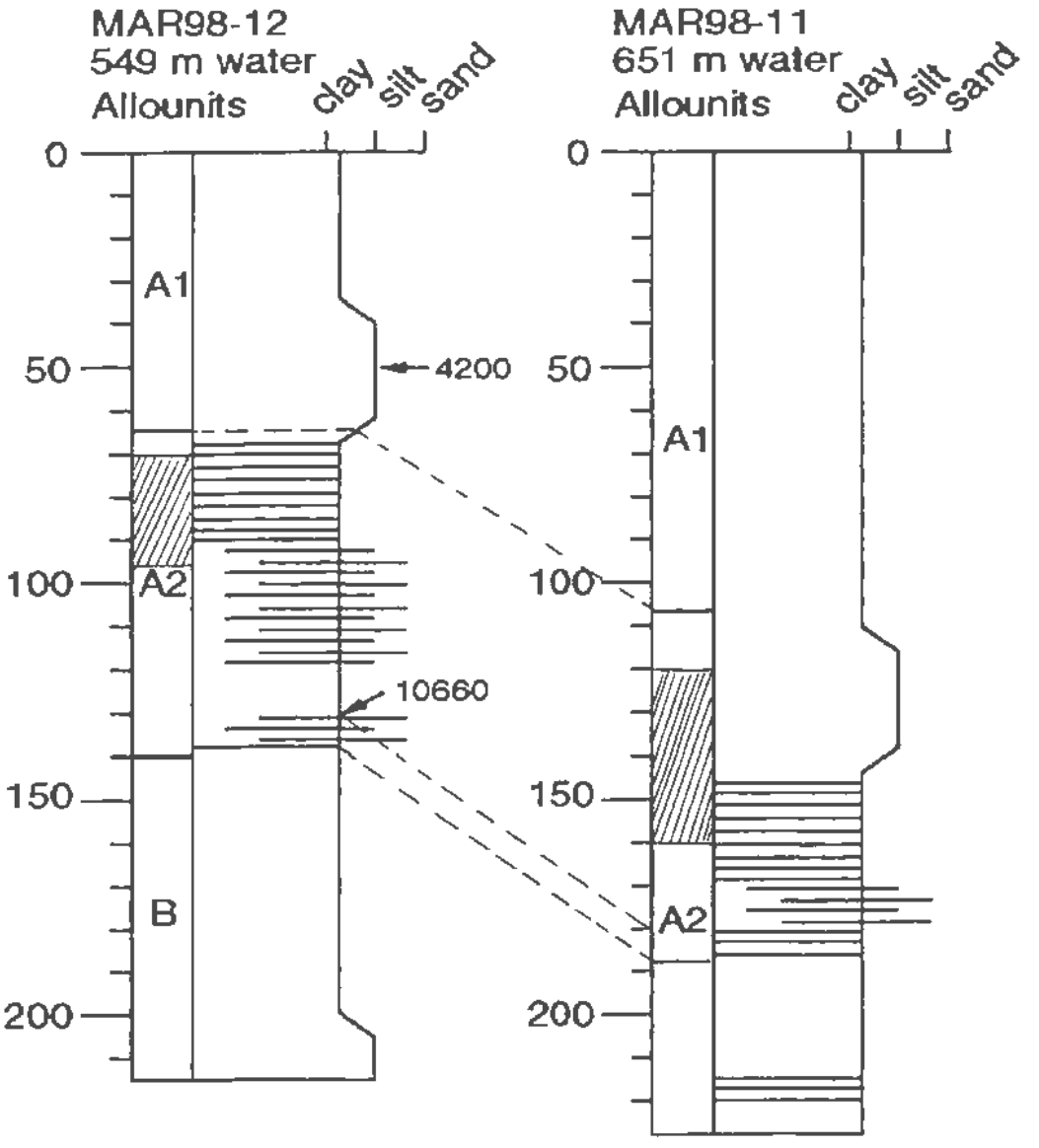


Figure 3.10: Lithostratigraphic correlation between core MAR98-11 and core MAR98-12. Dashed lines are tie lines indicating the most reasonable age correlation between the two cores. Arrows with numbers indicate radiocarbon ages in yr BP. Allostratigraphic units in MAR98-11 are different from that given by Hiscott and Aksu (2002). = True Sapropel (≥2%TOC). = Fine laminae.

mottles, grades to alternating layers of lighter and darker colors (Munsell 5Y2/1), and then to a distinctive faint parallel laminated interval downcore. Radiocarbon dates from core MAR98-12 for this "laminated sapropel" suggest that it was deposited from ~10.5-6 ka, at essentially the same time as sapropel S1 of the Aegean Sea (Aksu et al., 1995a,b).

The allounits for core MAR98-11 shown in Figure 3.10 do not correspond with the units given by Hiscott and Aksu (2002), who picked A2 to extend from 143 cm depth to the base of the core. In this thesis, however, Subunit A2 extends from 108 cm (where the upward transition to uniform and burrowed muds begins) to 185 cm. This interval also conforms to the definition of Subunit A2 in deep basins as an "organic-rich laminated sapropel" given by Aksu et al. (M1: 2002a).

At 185 cm in core MAR98-11, there is a sharp contact between laminated sediment with dark olive gray color (Munsell 5Y1/2) above, and lighter olive gray (Munsell 5Y5/2) silty mud with few laminations, very minor broken shells (~1 mm in size) and frequent monosulphide mottles (especially between 208 cm and 212 cm depth) below. This sharp contact is consistent with a facies change at ~12 ka observed by Hiscott and Aksu (2002) in other deep-water cores in the Marmara Sea and is assigned as the top of Allounit B. Allostratigraphic units in MAR98-11 are different from that given by Hiscott and Aksu (2002).

The improved correlation presented here is also based on new geochemical data, particularly total organic carbon (TOC). TOC values in Allounit B are consistent with the observations of Hiscott and Aksu (2002) for this unit, with lower TOC values ranging from 0.4 to 1.4% (TOC values <1% are observed in this unit for core MAR98-12).

CHAPTER FOUR

4.0 Discussion

Evaluation of paleoenvironmental conditions during sediment deposition requires the conversion of the multiproxy data depth to age domains. Age-related changes can then be potentially interpreted in terms of past environmental and/or climatic changes.

Linear extrapolations based on ^{14}C dates in the three Black Sea cores, assuming constant sedimentation rates, suggest ages of ~4820 yr BP and ~5074 for the tops (0 cm) of cores MAR005 and MAR00-8, respectively. However, the same process suggests that the core top of MAR00-6 has approximately a modern age. These values indicate that while MAR006 is characterized by continuous and uniform sediment deposition, the tops of cores MAR005 and MAR00-8 may be missing with ~5000 years hiatus immediately above the youngest ^{14}C dates in these cores. To evaluate these possibilities and to determine the reason for the discrepancies in apparent core-top ages from the same area of the southwestern Black Sea shelf, seismic reflection profiles crossing the Black Sea core sites were examined, although detailed interpretation of the grid of seismic data around the core sites is not within the scope of this thesis: it is carried out by Aksu et al. (2002).

Depth on a seismic profile is recorded as two-way travel time, rather than as elevation below a datum. Travel time is a function of distance travelled by the acoustic pulse and the velocity of sound in water and sediments. If the acoustic characteristics of the different sediment layers in a seismic profile are known, then travel time can be converted to an estimated depth in meters below the sea floor. An accurate time/depth conversion allows the correlation of seismic reflections to depths in cores.

Boomer seismic reflection profiles for the core sites are characterized by stratified seismic reflection configurations with two distinct units (Figures 4.1-4.3). There is an upper stratified unit (Unit 1) and a lower more transparent but stratified unit (Unit 2). These units are separated by a weak but continuous reflector that appears to be an erosional unconformity (Figures 4.1-4.3; Aksu et al., 2002). Seismic onlap over this surface (e.g. Figure 4.1) confirms the presence of an unconformity. Clearly, the unconformity between units 1 and 2 is diachronous. A similar ubiquitous but stronger, subaerial to possible near-shore submarine erosional unconformity has been reported previously across all Black Sea shelves (e.g. Okyar et al. 1994; Demirbağ et al. 1999; Aksu et al. 2002b), where it is buried by the thin mud drape of Unit 1.

Of the three Black Sea core sites, the Unit 1 drape is thinnest at core sites MAR00-5 and MAR00-8 (Figures 4.1, 4.3). The total thicknesses of the sediments overlying the erosional surface are estimated to be 40 cm and 10 cm for sites MAR00-5 and MAR00-8, respectively, based on two-way travel time/depth conversion in the seismic profiles. At these depths, the linear age models for the cores imply an age of ~5000 yr BP at the top of both cores (Figures 4.1, 4.3). The near absence of sediments younger than ~4900 yr BP in both cores suggests that there was either a substantial hiatus in sediment deposition and/or truncation of sediments by erosion. In contrast, a much thicker mud drape is present at site MAR00-6, and spans the time of the ~5000 yr BP unconformity with no obvious interruption of sedimentation. The 180 cm-thick mud drape recorded in the seismic profile at site MAR00-6 was not penetrated during recovery of the of the 132 cm core, so the age of the unconformity at this site is unknown.

The longer sedimentary record at site MAR00-6 might have resulted from greater

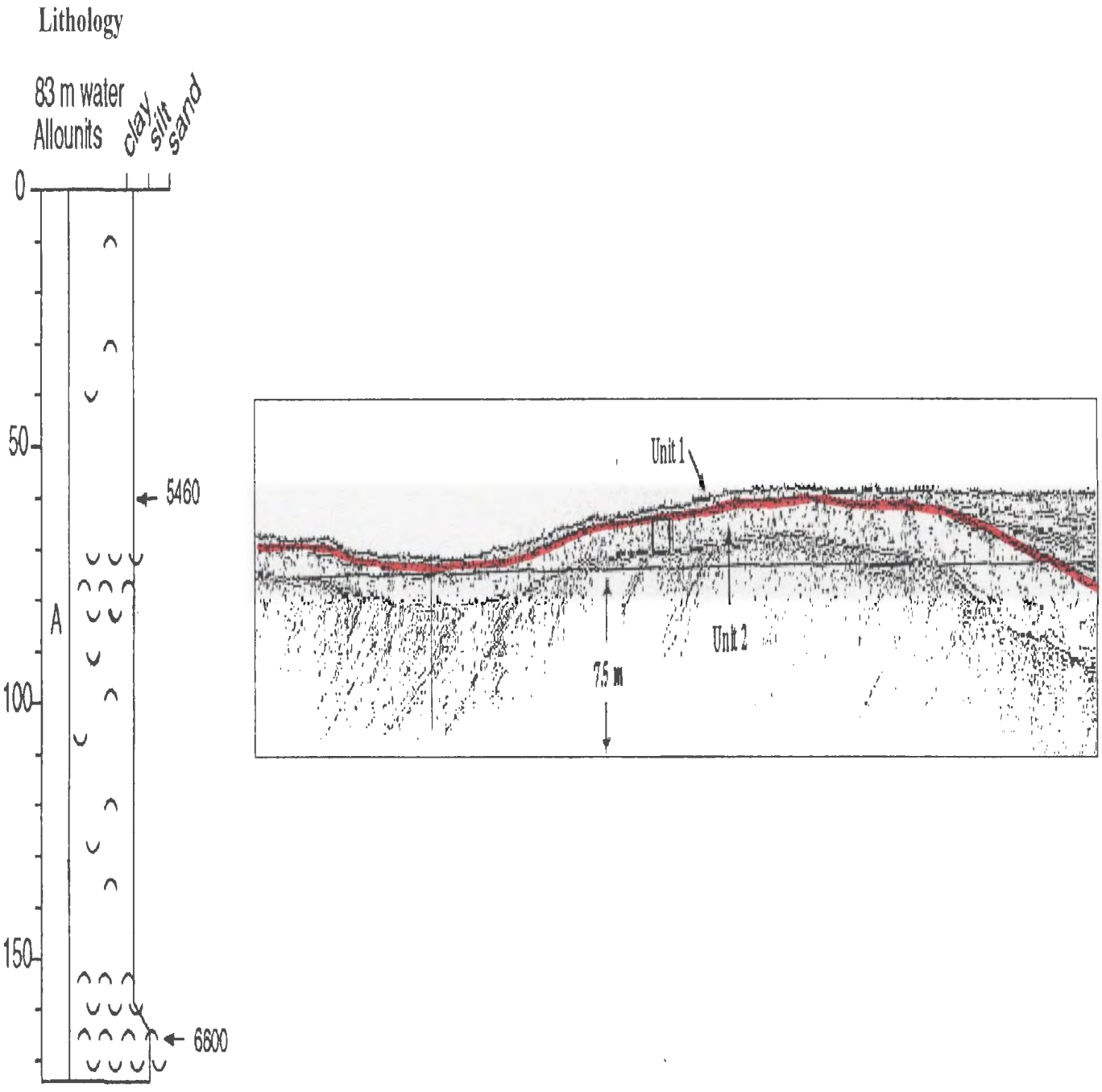


Fig. 4.1: Lithology (in cm depth) and Huntec DTS profile for site MAR00-5. The red line in the DTS profile represents the unconformity while the rectangular box represents the core length. Allounits are given by Hiscott and Aksu (2002). Arrows with numbers (5460 and 6600) are ^{14}C dates in yr BP.

Lithology

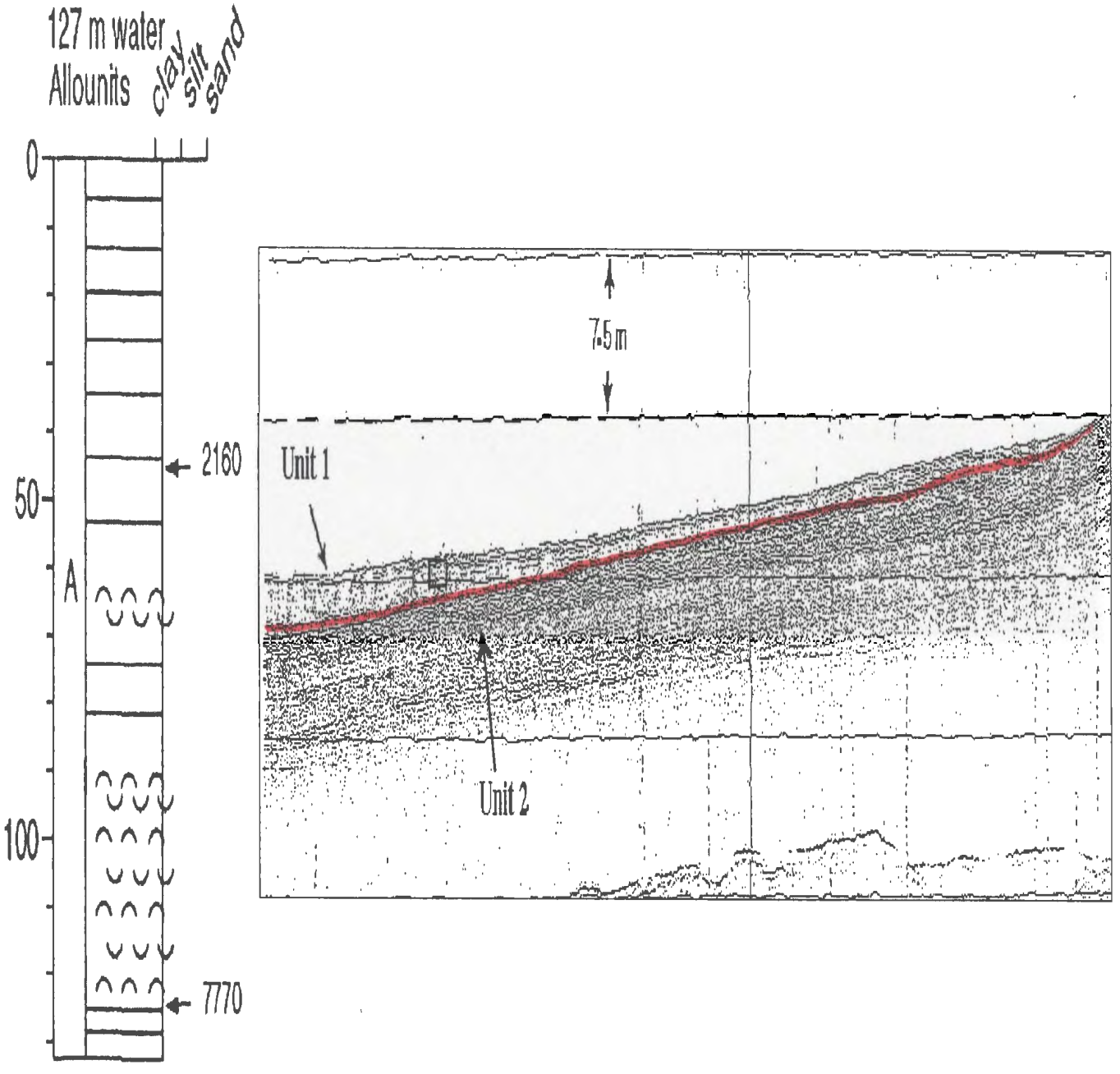


Fig. 4.2: Lithology (in cm depth) and Huntec DTS profile for site MAR00-6. The yellow in line the Huntec DTS profile represents the unconformity while the rectangular box represents the core length. Allounits are given by Hiscott and Aksu (2002). Arrows with numbers (2160 and 7770) are ^{14}C dates in yr BP.

Lithology

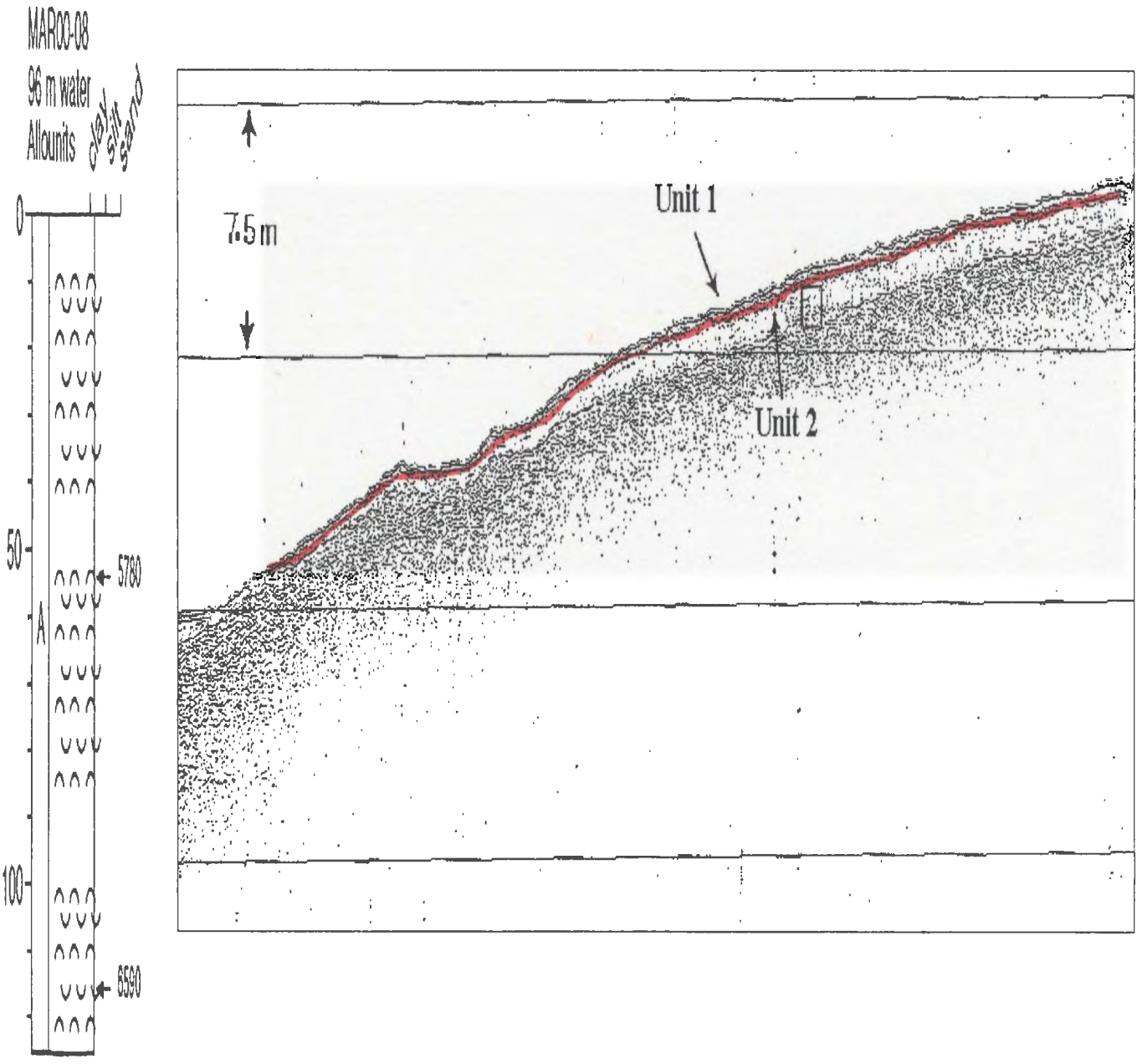


Fig. 4.3: Lithology (in cm depth) and Huntec DTS profile for site MAR00-8. The red line in the DTS profile represents the unconformity while the rectangular box represents the core length. Allounits are given by Hiscott and Aksu (2002). Arrows with numbers (5780 and 6590) are ^{14}C dates in yr BP.

water depth at this site, which is today 127 m. Even at a lower mid-Holocene sea level, wave energy beyond the shelf edge was apparently sufficiently low that mud deposition was continuous. The exact duration of the hiatus in cores MAR00-5 and MAR00-8 is unknown. Hence, emphasis will be placed on proxy data for the time interval before ~5000 yr BP. Younger events will be discussed only for core MAR00-6, with its better-constrained record of the more recent paleoceanography.

4.1 Age-Depth Conversion

Depths in the cores were transformed to ^{14}C ages by using two programs (Ager, Timer) in the Arand software package developed by CLIMAP at Brown University, Rhode Island (http://pixie.geo.brown.edu/esh/paleo/arand/arand.html). The Ager program assigns ages to the core depths where samples were collected and analyzed, by interpolating between known ages (e.g. ^{14}C ages) determined where datable material was found. The program requires an input file with a listing of sample depths (e.g. each 10 cm), proxy data for each sample, and a file containing the known depth-age relationships. The Ager output contains sample depths, the interpolated age for each sample, and a set of measured parameters for that sample. After being provided with starting time and time step (Δt) (200 years in this case) for its output, the Timer program interpolates the output from Ager to give a series of ages and associated estimates of each proxy variable at each time step. In this thesis, ^{14}C ages and not calendar years were used in the age-depth conversion. The tie points used for age-depth conversion are given in Table 4.1. The outputs of the age-to-depth conversion for all four cores are shown in Tables 4.2–4.5(a, b), while profiles of key proxy variables for all four cores are plotted against calculated ages in Figures 4.4–4.7.

Core	Depth (cm)	Age (^{14}C yr BP)
MAR00-5	40	5 246
MAR00-5	60	5 460
MAR00-5	70	5 566
MAR00-5	167	6 600
MAR00-6	45	2 160
MAR00-6	65	3 580
MAR00-6	90	5 356
MAR00-6	124	7 700
MAR00-8	10	5 205
MAR00-8	40	5 597
MAR00-8	54	5 780
MAR00-8	85	6 185
MAR00-8	100	6 380
MAR00-8	116	6 590
MAR98-11	108	6 400
MAR98-11	180	10 660

Table 4.1: Tie-points used for Age-Depth conversion

Age (^{14}C yr BP)	TOC_{OR} (wt %)	TOC (wt %)	TOC/TOC_{OR}	$\delta^{13}C$ (‰)	F_{TERR} (%)	Biogenic Opal (%)	Sulphur (wt %)	$\delta^{34}S$ (‰)	C/S
5000	3.37	2.00	0.59	-24.63	41.00	7.63	1.37	-27.06	1.46
5200	3.33	1.98	0.59	-24.63	41.00	8.06	1.35	-26.56	1.46
5400	3.50	1.99	0.56	-24.44	36.24	10.02	1.51	-14.69	1.31
5600	3.06	1.59	0.52	-25.02	50.42	1.24	1.47	-39.93	1.14
5800	2.21	1.66	0.76	-25.43	60.57	2.22	0.47	-38.63	3.54
6000	3.23	1.86	0.58	-26.46	86.95	2.12	1.21	-36.26	1.83
6200	3.78	2.04	0.54	-26.04	75.96	1.93	1.75	-33.16	1.18
6400	3.93	1.87	0.48	-26.11	78.00	1.75	2.07	-30.60	0.90

Table 4.2: Age-depth conversion output for proxies measured in Black Sea core MAR00-5 for the time interval before ~5000 yr BP.

Age (^{14}C yr BP)	TOC_{OR} (wt %)	TOC (wt %)	TOC/TOC_{OR}	$\delta^{13}C$ (‰)	F_{TERR} (%)	Biogenic Opal (%)	Sulphur (wt %)	$\delta^{34}S$ (‰)	C/S
0	3.12	**2.62**	0.84	-24.77	44.00	10.96	0.50	-14.08	5.27
200	3.09	**2.62**	0.85	-24.80	44.83	9.75	0.47	-13.51	5.68
400	3.05	**2.62**	0.86	-24.83	45.67	8.54	0.43	-12.93	6.09
600	2.87	**2.47**	0.86	-24.93	48.50	7.32	0.40	-14.16	5.93
800	2.59	**2.23**	0.86	-25.09	52.67	6.08	0.36	-16.61	5.40
1000	2.33	**2.00**	0.86	-25.23	56.08	5.48	0.33	-18.52	5.00
1200	2.15	1.84	0.86	-25.26	56.50	7.44	0.32	-18.34	5.17
1400	1.98	1.67	0.85	-25.28	56.92	9.40	0.30	-18.17	5.33
1600	2.00	1.67	0.84	-25.41	60.33	7.21	0.33	-20.75	5.06
1800	2.08	1.71	0.83	-25.57	64.50	3.99	0.37	-24.02	4.68
2000	2.20	1.76	0.81	-25.62	65.92	1.97	0.44	-27.88	4.22
2200	2.40	1.85	0.78	-25.52	63.24	1.77	0.55	-32.61	3.63
2400	2.60	1.93	0.75	-25.43	60.55	1.57	0.66	-37.34	3.04
2600	2.75	1.96	0.72	-25.41	60.08	1.82	0.78	-40.70	2.57
2800	2.83	1.92	0.68	-25.51	62.61	2.68	0.91	-42.20	2.25
3000	2.92	1.88	0.65	-25.61	65.15	3.55	1.03	-43.70	1.94
3200	3.00	1.85	0.61	-25.71	67.68	4.41	1.16	-45.20	1.62
3400	3.15	1.91	0.61	-25.60	65.04	3.91	1.24	-45.48	1.55
3600	3.30	1.98	0.60	-25.46	61.66	3.22	1.32	-45.59	1.51
3800	3.46	2.06	0.59	-25.32	58.28	2.52	1.40	-45.70	1.48
4000	3.50	2.06	0.59	-25.30	57.83	2.30	1.44	-45.58	1.42
4200	3.32	1.91	0.57	-25.53	63.45	3.08	1.41	-45.00	1.34
4400	3.14	1.75	0.56	-25.75	69.08	3.86	1.39	-44.42	1.25
4600	2.95	1.60	0.54	-25.98	74.71	4.64	1.36	-43.84	1.17
4800	3.38	1.81	0.54	-25.78	69.71	4.27	1.57	-43.52	1.15
5000	3.99	**2.13**	0.54	-25.45	61.54	3.54	1.86	-43.28	1.15
5200	4.60	**2.46**	0.53	-25.12	53.37	2.82	2.15	-43.04	1.14
5400	5.08	**2.73**	0.53	-24.92	48.55	2.46	2.36	-42.57	1.16
5600	5.09	**2.82**	0.55	-25.21	55.59	3.35	2.29	-41.31	1.24
5800	5.11	**2.90**	0.57	-25.49	62.63	4.25	2.21	-40.05	1.32
6000	5.12	**2.99**	0.58	-25.78	69.68	5.14	2.14	-38.79	1.40
6200	5.01	**2.94**	0.59	-25.98	74.64	4.65	2.08	-38.15	1.41
6400	4.83	**2.81**	0.58	-26.14	78.59	3.47	2.03	-37.81	1.39
6600	4.66	**2.69**	0.58	-26.30	82.53	2.29	1.98	-37.48	1.36
6800	4.52	**2.60**	0.57	-26.43	85.76	1.32	1.92	-36.97	1.36
7000	4.61	**2.75**	0.59	-26.35	83.79	1.88	1.86	-35.13	1.49
7200	4.71	**2.90**	0.61	-26.28	81.82	2.45	1.81	-33.29	1.62

Table 4.3: Age-depth conversion output for proxies measured in Black Sea core MAR00-6. Shading highlights results for the time interval before ~5000 yr BP. The bold figures represent intervals with two or more successive values of TOC ≥2%.

Age (^{14}C yr BP)	TOC_{OR} (wt %)	TOC (wt %)	TOC/TOC_{OR}	$\delta^{13}C$ (‰)	F_{TERR} (%)	Biogenic Opal (%)	Sulphur (wt %)	$\delta^{34}S$ (‰)	C/S
5000	3.15	1.80	0.57	-25.23	55.84	10.49	1.35	-33.57	1.34
5200	3.13	1.79	0.57	-25.24	56.00	10.69	1.34	-33.24	1.34
5400	3.64	**2.14**	0.60	-24.84	46.58	9.32	1.50	-38.23	1.54
5600	5.53	**3.01**	0.54	-24.10	27.21	13.58	2.53	-31.88	1.20
5800	4.35	**2.50**	0.57	-24.67	42.09	9.78	1.86	-31.86	1.35
6000	4.94	**2.98**	0.61	-24.22	30.44	15.29	1.95	-28.45	1.52
6200	4.25	**2.54**	0.60	-25.19	55.15	14.09	1.71	-30.05	1.50
6400	4.15	**2.65**	0.64	-25.27	56.86	6.97	1.49	-28.64	1.80

Table 4.4: Age-depth conversion output for proxies measured in Black Sea core MAR00-8 for the time interval before ~5000 yr BP. The bold figures represent intervals with two or more successive values of TOC ≥2%.

Age (^{14}C yr BP)	TOC_{OR} (wt %)	TOC (wt %)	TOC/TOC_{OR}	$\delta^{13}C$ (‰)	F_{TERR} (%)	Biogenic Opal (%)	Sulphur (wt %)	$\delta^{34}S$ (‰)	C/S
0	1.31	1.25	0.95	-23.58	15.00	1.25	0.06	-1.19	20.83
200	1.29	1.23	0.95	-23.63	16.01	1.91	0.06	-2.69	20.44
400	1.26	1.20	0.95	-23.68	17.02	2.56	0.06	-4.19	20.05
600	1.24	1.18	0.95	-23.72	17.78	3.19	0.06	-5.88	19.56
800	1.28	1.20	0.94	-23.47	11.70	3.20	0.08	-12.72	16.70
1000	1.31	1.21	0.93	-23.22	5.62	3.20	0.09	-19.55	13.83
1200	1.34	1.23	0.92	-23.01	0.56	3.19	0.11	-25.92	11.16
1400	1.27	1.16	0.92	-23.31	7.98	2.95	0.11	-26.61	10.90
1600	1.20	1.10	0.91	-23.61	15.40	2.71	0.10	-27.30	10.63
1800	1.14	1.04	0.91	-23.86	21.74	2.54	0.10	-27.86	10.50
2000	1.14	1.04	0.92	-23.77	19.38	2.93	0.09	-27.40	11.42
2200	1.13	1.05	0.92	-23.68	17.01	3.32	0.09	-26.94	12.34
2400	1.15	1.06	0.93	-23.60	14.85	3.51	0.08	-26.78	12.90
2600	1.26	1.16	0.92	-23.55	13.84	2.58	0.11	-28.29	11.44
2800	1.38	1.25	0.91	-23.50	12.82	1.65	0.13	-29.80	9.99
3000	1.47	1.32	0.90	-23.48	12.56	1.12	0.15	-30.83	8.97
3200	1.49	1.35	0.91	-23.60	15.60	2.33	0.14	-29.73	9.91
3400	1.50	1.37	0.91	-23.73	18.63	3.55	0.13	-28.63	10.85
3600	1.53	1.40	0.92	-23.83	21.30	4.59	0.13	-28.29	11.16
3800	1.63	1.46	0.90	-23.89	22.65	4.97	0.18	-30.64	9.26
4000	1.74	1.51	0.88	-23.94	24.00	5.36	0.23	-32.99	7.37
4200	1.82	1.55	0.85	-24.02	25.96	5.74	0.27	-35.00	5.78
4400	1.87	1.55	0.83	-24.17	29.67	6.07	0.32	-36.05	5.09
4600	1.92	1.56	0.81	-24.32	33.38	6.41	0.37	-37.10	4.39
4800	1.93	1.55	0.81	-24.40	35.50	6.86	0.38	-37.31	4.21
5000	1.84	1.52	0.84	-24.35	33.81	7.61	0.32	-35.51	5.26
5200	1.74	1.49	0.86	-24.29	32.12	8.36	0.25	-33.71	6.30
5400	1.70	1.49	0.88	-24.25	31.11	8.59	0.22	-32.87	6.88
5600	1.77	1.53	0.87	-24.27	31.45	7.80	0.24	-33.95	6.53
5800	1.84	1.58	0.86	-24.28	31.79	7.00	0.26	-35.02	6.18
6000	1.97	1.65	0.85	-24.37	34.13	6.00	0.32	-36.22	5.58
6200	2.20	1.75	0.81	-24.59	39.87	4.65	0.45	-37.63	4.57
6400	2.43	1.86	0.77	-24.81	45.61	3.31	0.57	-39.04	3.55

Table 4.5 (a): Age-depth conversion output for proxies measured in Marmara Sea core MAR98-11 for the time interval for the time interval 6400 yr BP to present.

Age (^{14}C yr BP)	TOC_{OR} (wt %)	TOC (wt %)	TOC/TOC_{OR}	$\delta^{13}C$ (‰)	F_{TERR} (%)	Biogenic Opal (%)	Sulphur (wt %)	$\delta^{34}S$ (‰)	C/S
6600	2.76	**2.04**	0.74	-24.94	48.86	2.45	0.72	-39.85	2.88
6800	3.21	**2.33**	0.73	-24.94	48.52	2.30	0.89	-39.80	2.69
7000	3.67	**2.61**	0.72	-24.93	48.19	2.14	1.06	-39.75	2.51
7200	3.78	**2.67**	0.71	-24.94	48.46	2.46	1.10	-39.70	2.42
7400	3.46	**2.45**	0.71	-24.97	49.47	3.35	1.00	-39.67	2.45
7600	3.13	**2.23**	0.71	-25.00	50.48	4.24	0.90	-39.64	2.48
7800	3.08	**2.17**	0.70	-25.10	52.82	4.39	0.91	-39.43	2.41
8000	3.30	**2.27**	0.69	-25.26	56.55	3.76	1.03	-39.03	2.24
8200	3.53	**2.37**	0.68	-25.42	60.27	3.14	1.15	-38.63	2.08
8400	3.70	**2.42**	0.66	-25.39	59.65	3.57	1.28	-38.07	1.91
8600	3.82	**2.42**	0.63	-25.20	55.26	4.90	1.40	-37.37	1.75
8800	3.94	**2.41**	0.61	-25.02	50.87	6.24	1.53	-36.67	1.59
9000	3.96	**2.36**	0.59	-25.14	53.86	6.28	1.60	-36.70	1.47
9200	3.91	**2.27**	0.58	-25.48	62.30	5.35	1.64	-37.27	1.39
9400	3.86	**2.18**	0.57	-25.82	70.75	4.43	1.68	-37.85	1.30
9600	3.70	**2.11**	0.57	-25.97	74.41	3.95	1.58	-37.85	1.35
9800	3.46	**2.05**	0.59	-26.00	75.09	3.77	1.41	-37.50	1.48
10000	3.22	1.98	0.61	-26.03	75.76	3.58	1.24	-37.14	1.61
10200	3.00	1.81	0.60	-26.06	76.66	4.02	1.19	-37.54	1.53
10400	2.79	1.59	0.56	-26.10	77.68	4.80	1.20	-38.35	1.32
10600	2.57	1.36	0.52	-26.14	78.69	5.59	1.22	-39.16	1.12
10800	2.48	1.28	0.51	-26.12	78.29	5.84	1.20	-39.17	1.07
11000	2.45	1.27	0.52	-26.08	77.27	5.87	1.18	-38.84	1.08
11200	2.41	1.25	0.52	-26.03	76.25	5.89	1.16	-38.51	1.09
11400	2.42	1.24	0.51	-26.22	80.83	5.21	1.18	-38.39	1.06
11600	2.45	1.23	0.50	-26.48	87.27	4.29	1.22	-38.34	1.02
11800	2.48	1.22	0.49	-26.75	93.71	3.37	1.25	-38.29	0.98
12000	2.53	1.27	0.50	-26.83	95.80	3.52	1.26	-38.48	1.01
12200	2.60	1.34	0.51	-26.86	96.80	3.92	1.26	-38.72	1.07
12400	2.67	1.41	0.53	-26.89	97.80	4.33	1.26	-38.97	1.12
12600	2.45	1.29	0.52	-26.67	92.03	4.37	1.16	-38.04	1.10
12800	2.16	1.12	0.52	-26.38	84.58	4.33	1.04	-36.82	1.07

Table 4.5(b): Age-depth conversion output for proxies measured in Marmara Sea core MAR98-11 for the time interval 128000 yr BP to 6600 yr BP. The bold figures represent intervals with two or more successive values of TOC ≥2%.

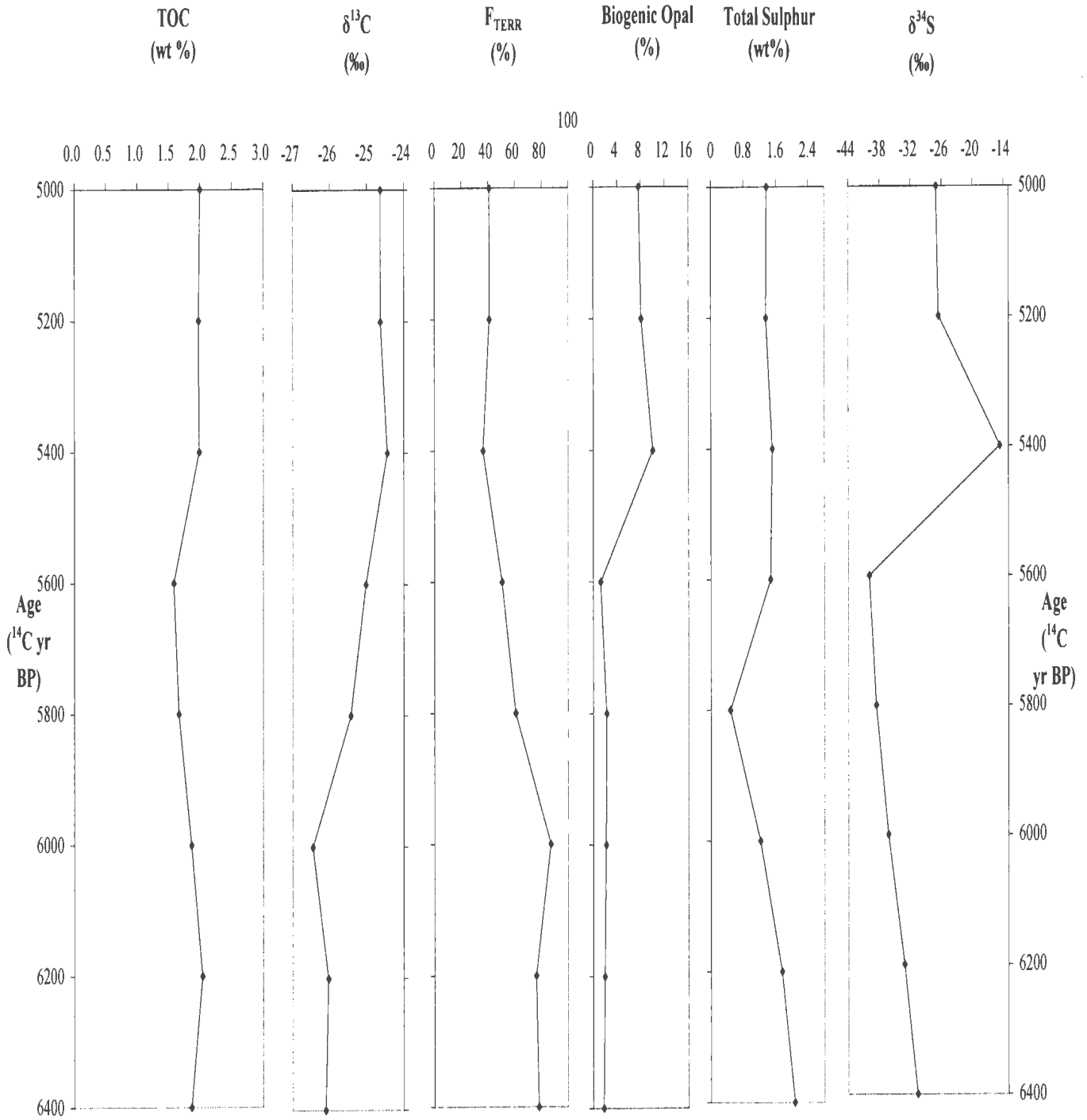


Fig 4.4: Age profiles (as uncalibrated conventional ^{14}C dates in yr BP) of total organic carbon (TOC), carbon isotope composition ($\delta^{13}C$), terrigenous organic carbon fraction (F_{TERR}), biogenic opal (silica), total sulphur (TS), and sulphur isotopic composition ($\delta^{34}S$) for Black Sea core MAR00-5.

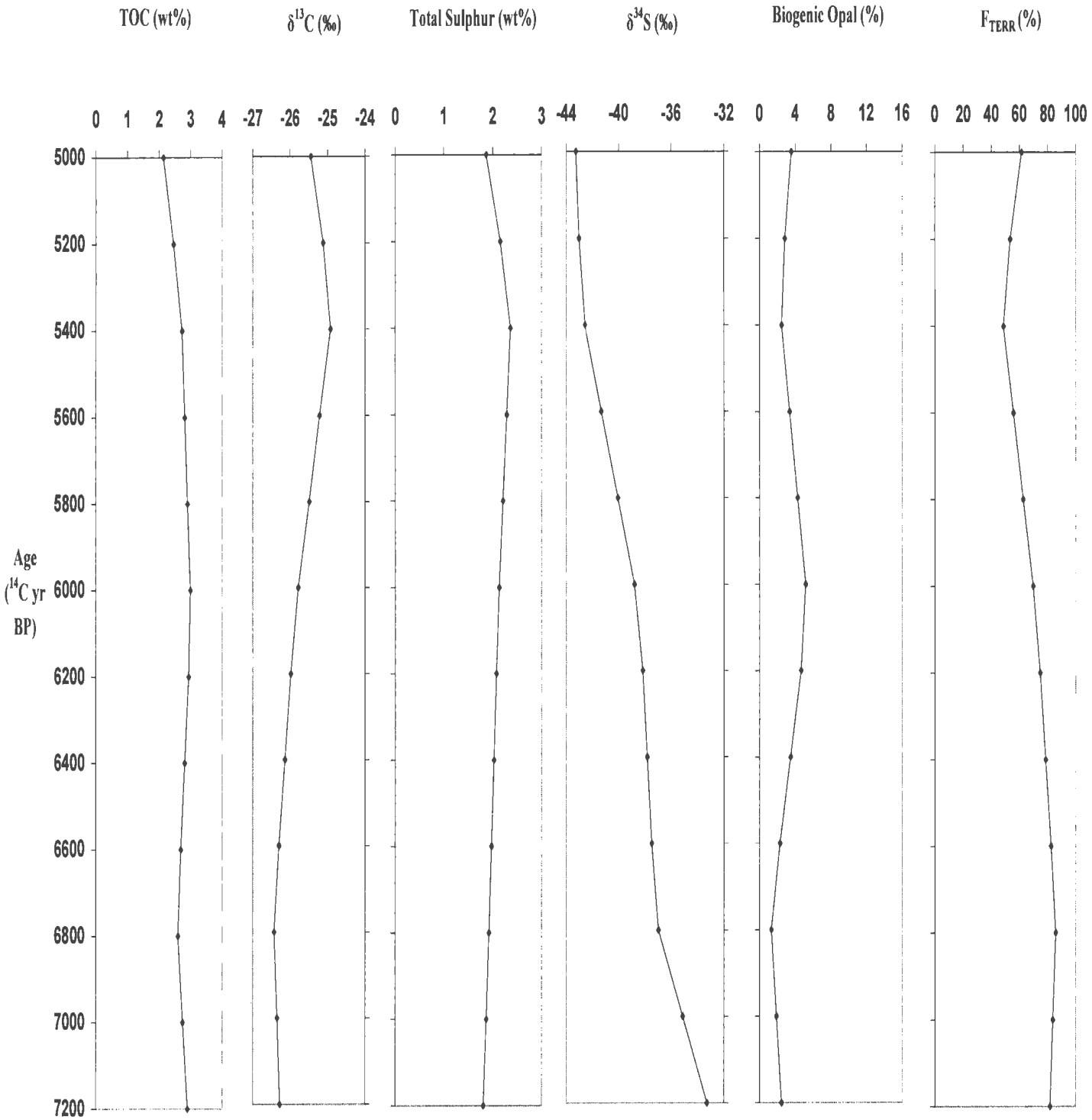


Fig 4.5 Age profiles (as uncalibrated conventional ^{14}C dates in yr BP) of total organic carbon (TOC), carbon isotope composition ($\delta^{13}C$), total sulphur (TS), sulphur isotopic composition ($\delta^{34}S$), biogenic opal (silica), and terrigenous organic carbon fraction (F_{TERR}) in core MAR00-6 sediments older than 5000 yr BP.

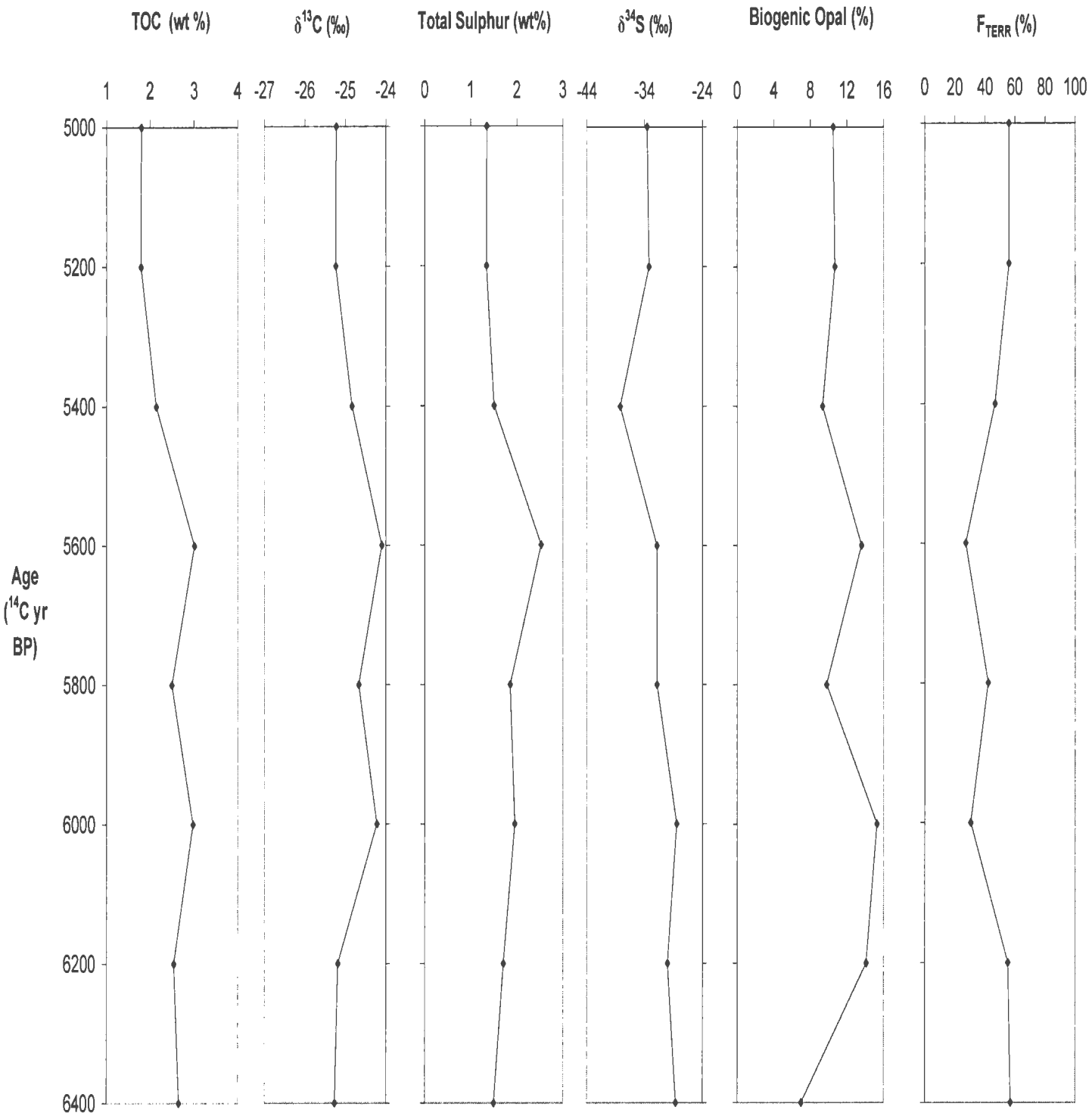


Fig 4.6: Age profiles (as uncalibrated conventional ^{14}C dates in yr BP) of total organic carbon (TOC), carbon isotope composition ($\delta^{13}C$), total sulphur (TS), sulphur isotopic composition ($\delta^{34}S$), biogenic opal (silica), and terrigenous organic carbon fraction (F_{TERR}) for core MAR00-8 older than 5000 yr BP.

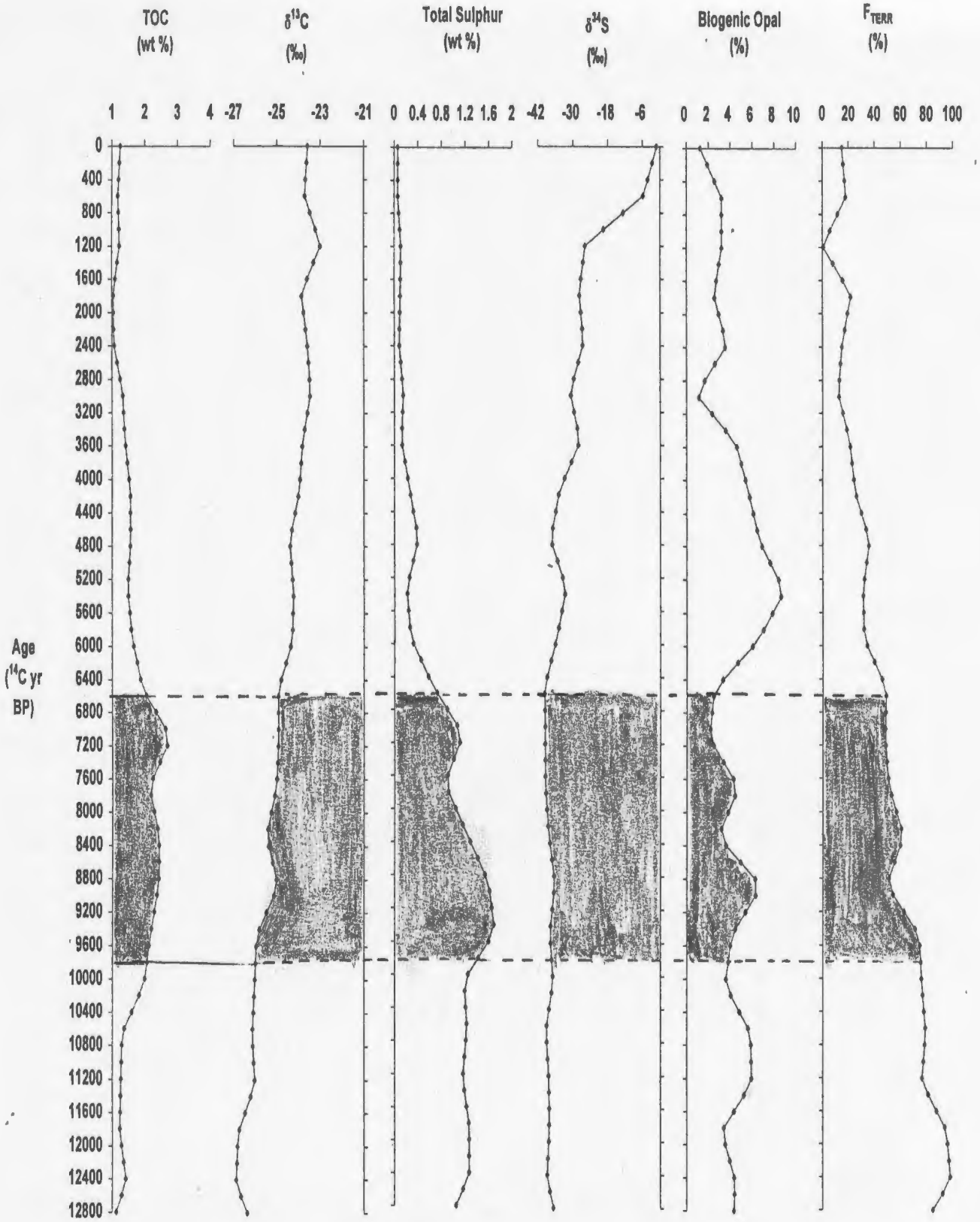


Fig 4.7: Age profiles (as uncalibrated conventional ^{14}C dates in yr BP) of total organic carbon (TOC), carbon isotope composition ($\delta^{13}C$), total sulphur (TS), sulphur isotopic composition ($\delta^{34}S$), biogenic opal (silica), and terrigenous organic carbon fraction (F_{TERR}) for core MAR98-11. Intervals with two or more successive values of TOC $\geq$2% are indicated in the shaded area.

4.2 Black and Marmara Seas

Sediments from the Black Sea were divided into a three-unit Holocene stratigraphy by Ross and Degens (1974). Their units I and II were interpreted as marine deposits while Unit III sediments were found to be lacustrine and represent the most recent low-salinity lake stage of the Black Sea. Although Ross and Degens (1974) reported that Unit I and the organic-carbon-rich Unit II sapropel were deposited between 0-3000 yr BP and 3000-7000 yr BP, respectively, the exact dating of these units is still controversial. According to more recent studies based on radiocarbon dating (Jones and Gagnon, 1994), varve counting (Hay et al., 1991) and sediment geochemical studies (Arthur et al., 1994; de Leeuw et al., 1981), estimates of the age of the Unit I-II boundary range from 1630 yr BP to 2700 yr BP. Jones and Gagnon (1994) proposed an age of ~7000 to 7500 yr BP for the Unit II-III boundary.

4.2.1 Southwestern Black Sea

Most of the previous work on the Black Sea shelf has been done in the northwest (e.g. Lein et al., 2002; Wijsman et al., 1999; Muramoto et al., 1991). However, this thesis considers sediment cores from the southwestern Black Sea shelf. The sediments in the southwestern Black Sea shelf are mainly dominated by shell-rich horizons interbedded with burrowed terrigenous muds, presumably supplied in part by local rivers. Furthermore, since little tectonic activity has occurred along the southwestern Black Sea shelf (Aksu et al., 2002b; Hiscott and Aksu, 2002), glacio-eustatic sea-level variations probably controlled sediment accumulation, although Ryan et al. (2003a) have also proposed a post-glacial sea-level fall to ~ -100 m followed by a rapid inundation by Mediterranean water at ~8400 yr BP.

The gravity cores collected from the study area cover a range of depths from the outer shelf (MAR00-05 – 83 m water depth) to the toe of the lowstand shelf-edge deltas (MAR00-06 – 127 m water depth; and MAR00-08 – 96 m water depth). Apart from a radiocarbon date of 7770 yr BP near the base of core MAR00-6, the three southwestern Black Sea cores are no older than 6500 yr BP. Based on conversion of depths to ages performed earlier, the sediment cores analyzed in this thesis correspond mainly to Unit I and Unit II of Ross and Degens (1974). Hence several thousands of years of deposits, dating from 10500 to 6500 yr BP, were not measured in these cores. The lack of accumulation of 10500 to 6500 yr BP sediments in this area has been largely attributed to wave erosion during the early stages of transgression (Hiscott and Aksu, 2002).

4.2.2 Marmara Sea

Previous studies (e.g. Çağatay et al., 2000) have subdivided the late glacial to Holocene sediments of the Marmara Sea into an upper marine and a lower lacustrine unit. The marine/lacustrine boundary has been dated to ~ 12000 yr BP (Hiscott and Aksu, 2002; Aksu et al., 2002a; GSA Today). Based on conversion of depths to ages (Table 4.4), the Marmara Sea core MAR98-11 analyzed in this thesis was deposited after the transgression of the Marmara Sea by Mediterranean waters via the Aegean Sea at ~12000 yr BP and consists relatively of the upper marine unit. After the last deglaciation, sea-level rise began ~12000 yr BP in the Marmara Sea when the sill at the Dardanelles was breached. The salinity increase during this marine transgression was gradual. Salinity reconstructions by Mudie et al., (2004) indicate that the Marmara Sea was a brackish or low-salinity sea by ~11000 yr BP. Within the time interval 12800-10600 yr BP, there was neither an outflow from the Black Sea to the Marmara Sea nor a marine incursion into the

Black Sea since the sill depth of the Bosphorus is ~30 m shallower than that of the Dardanelles. Thus, the marine intrusion of Mediterranean water occurred earlier (~12000 yr BP) in the Marmara Sea than in the Black Sea (Çağatay et al., 2000), the late Quaternary marine record of the Marmara Sea is longer.

By ~10500 yr BP, a large freshwater flux from major European rivers and excess precipitation swelled the Black Sea so that it began to spill over into the Marmara Sea (Hiscott et al., in press). The brackish water from the Black Sea formed a thick surface layer over higher salinity Mediterranean waters that occupied the deeper portions of the Marmara Sea basins. These distinct water masses are today separated by a sharp halocline, and the same conditions is inferred for ~10500 yr BP (Aksu et al., 2002a). Even though both water masses entering the Marmara Sea were well oxygenated, subhalocline waters became oxygen deficient, with oxygen deficiency increasing with depth as a result of poor vertical mixing (Aksu et al., 2002; Kaminski et al., 2002). Çağatay et al. (2000) had earlier stated that the deposition of sapropel M1 in the Marmara Sea was the result of stratification of the water column by ~10500 yr BP, Kaminski et al. (2002) placed the initiation of sustained two-way water flow in the Bosphorus Strait at ~8500 yr BP.

4.3 Organic Matter Source Characterization

Bulk $\delta^{13}C$ values of sedimentary organic matter are useful in discriminating between terrestrial and marine organic matter (Peters et al., 1978; Wada et al., 1987; Jasper and Gagosian, 1990). Terrestrial plants fix atmospheric CO_2 during photosynthesis. The extent of carbon isotopic fractionation during photosynthesis depends on the metabolic pathway used. This results in the distinction between different classes of terrestrial plants based on $\delta^{13}C$ values. The C3 (or Calvin-Benson) photosynthetic

pathway involves the maximum ^{13}C ^{12}C fractionation and results in plants having $\delta^{13}C$ values of -23 to -35‰, with an average $\delta^{13}C$ value of -26‰ (Deines, 1981). Terrestrial plants that utilize the C4 (or Hatch-Slack) pathway exhibit a relatively smaller carbon isotopic fractionation, which results in $\delta^{13}C$ values of -9 to -16‰, with an average $\delta^{13}C$ value of -13‰ (Deines, 1981). C3 plants include most of the higher plants while C4 plants comprise mostly the grasses. A third group of plants, the succulents found in water-limited environments, utilize both C3 and C4 photosynthetic pathways, known as crassulacean acid metabolism, and are thus referred to as CAM plants. Generally, terrestrial organic matter typically has $\delta^{13}C$ values more negative than -23‰, whereas marine organic matter typically has values less negative than -23‰ (Meyers, 1994). Typical ranges of $\delta^{13}C$ values for both sources are shown in Table 4.6 and Figure 4.8.

4.3.1 Black Sea Cores

Similar to most continental shelf areas, proximity to land as well as river discharges would have resulted in the introduction of large quantities of terrestrial carbon to core sites MAR00-5, MAR00-6 and MAR00-8 on the southwestern Black Sea shelf. Terrestrial material delivered onto shallow continental shelf waters is usually nutrient-rich, resulting in a high organic productivity. In addition, the range of $\delta^{13}C$ values from ~26‰ to ~-23‰ for the TOC in the Black Sea cores (Figure 4.9) covers much of the range reported for marine algae and part of C3 land plants (Figure 4.8).

Organic Matter Type	Total $\delta^{13}C$ range (‰)	$\delta^{13}C$ range (‰)
Terrestrial C4 plants (e.g. trees)	-6 to -23	-10 to -14
Terrestrial C3 plants (e.g. grass)	-23 to -35	-23 to -31
Marine Plankton		
Low to middle latitudes	-13 to -31	-18 to -24
High latitude (Antarctic)		-25 to -31

Table 4.6: Typical ranges of $\delta^{13}C$ for marine and terrestrial organic matter (modified from Table 23.2 of Tyson, 1995)

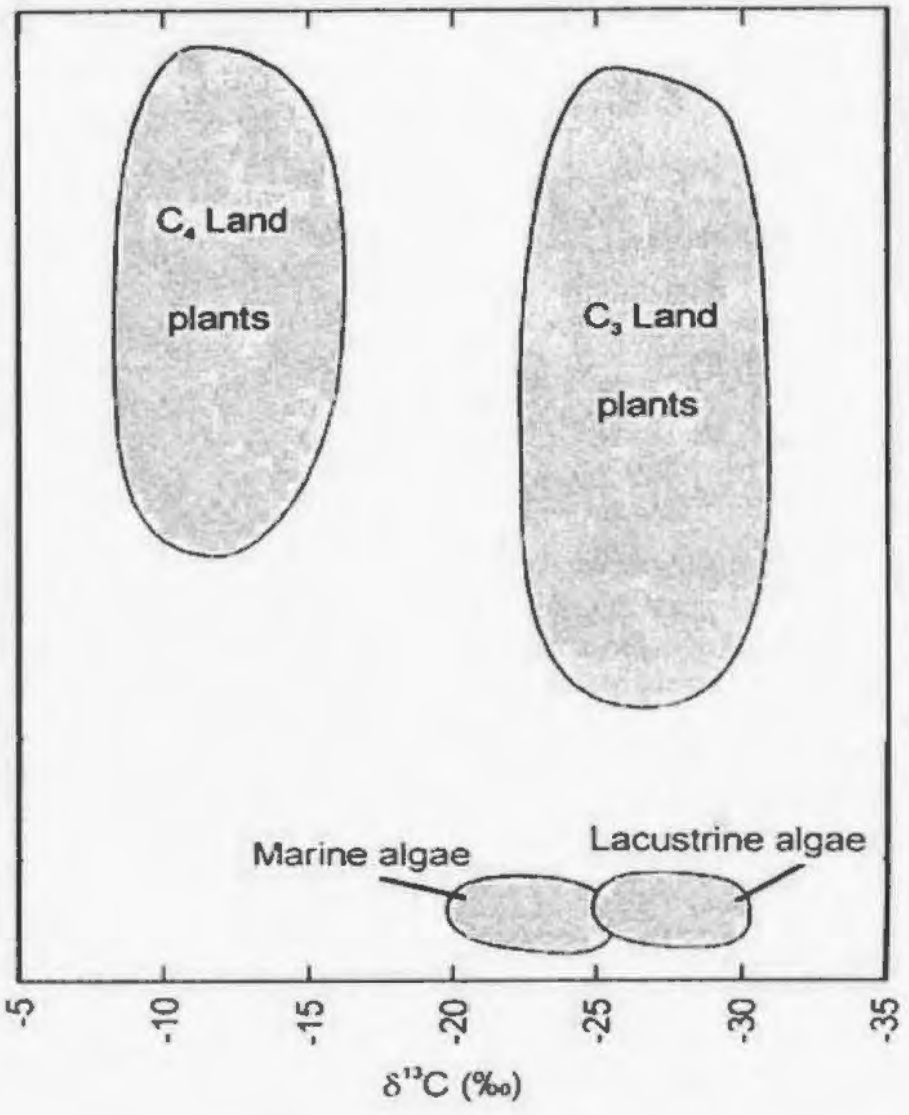


Figure 4.8: Typical ranges of $\delta^{13}C$ for marine algae, lacustrine algae, C4 and C3 plants (modified from Meyers, 1994).

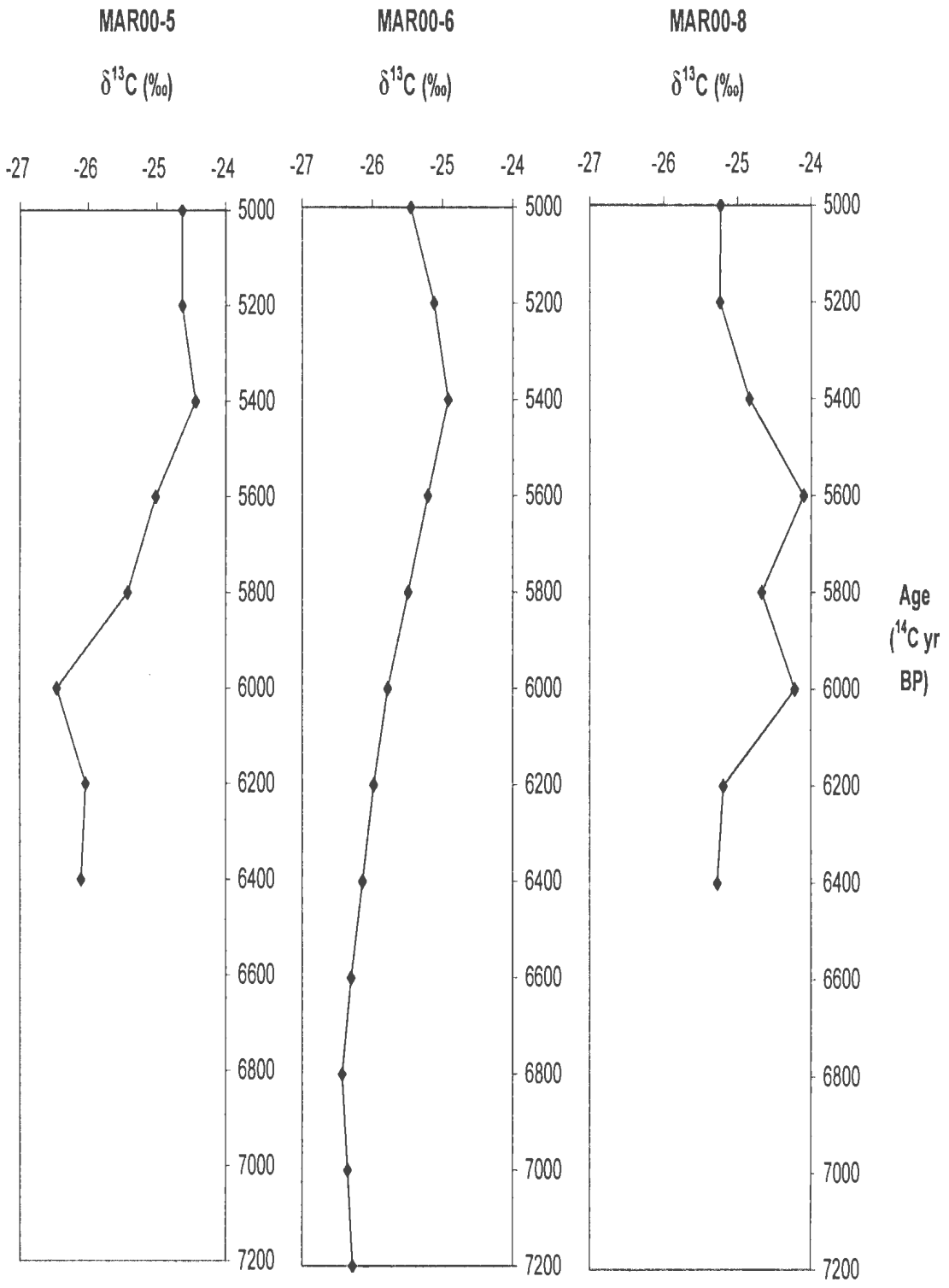


Figure 4.9: Age Profiles (as uncalibrated conventional ^{14}C ages) of $\delta^{13}C$ values for sediments older than 5000 yr BP in the Black Sea cores MAR00-5, MAR00-6 and MAR00-8.

It is possible to interpret the range of carbon isotope values in terms of mixing of isotopically light land-derived material with isotopically heavier autochthonous marine primary production. Such mixing is common in coastal marine environments (Cowie et al., 1995; Galimov et al., 2002 and references therein). There are however distinct differences in terrestrial components, primary productivity and carbon isotopic signatures between the cores.

Terrestrial organic matter predominates in core MAR00-6 from ~7200–5000 yr BP and in core MAR00-5 from ~6400–5600 yr BP (Figure 4.10). This observation is consistent with $\delta^{13}C$ values of –24.92 to –26.46‰ (Figure 4.9) and relatively low biogenic opal contents (Figure 4.11) in these time intervals. There is however more terrestrial contribution to the TOC pool in MAR00-6 as shown by relatively higher F_{TFRR} (Figure 4.10) and relatively lower biogenic opal contents in the core (Figure 4.11). In addition, the TOC content of MAR00-6 is much higher than in MAR00-5 (Figure 4.12) even though the degree of organic matter preservation (TOC/TOC_{OR}) is nearly the same in both cores (Figure 4.13). A plausible explanation for this is that, although both cores had high amounts of terrestrial organic carbon, there was generally a higher contribution from land-derived sources to the TOC content in MAR00-6. In core MAR00-5, there was a greater amount of marine organic matter as shown by the upward increase in $^{13}C/^{12}C$ ratio in core MAR00-5 (Figure 4.9). Such increases in $\delta^{13}C$ values have been reported to represent organic matter deposition during periods of ehnanced productivity (Calver and Pedersen, 1993). These data suggests that diagenesis has altered the carbon isotopic composition and reduced the TOC content more in core MAR00-5, since marine organic matter is more labile and more susceptible to diagenetic effects than terrestrial organic

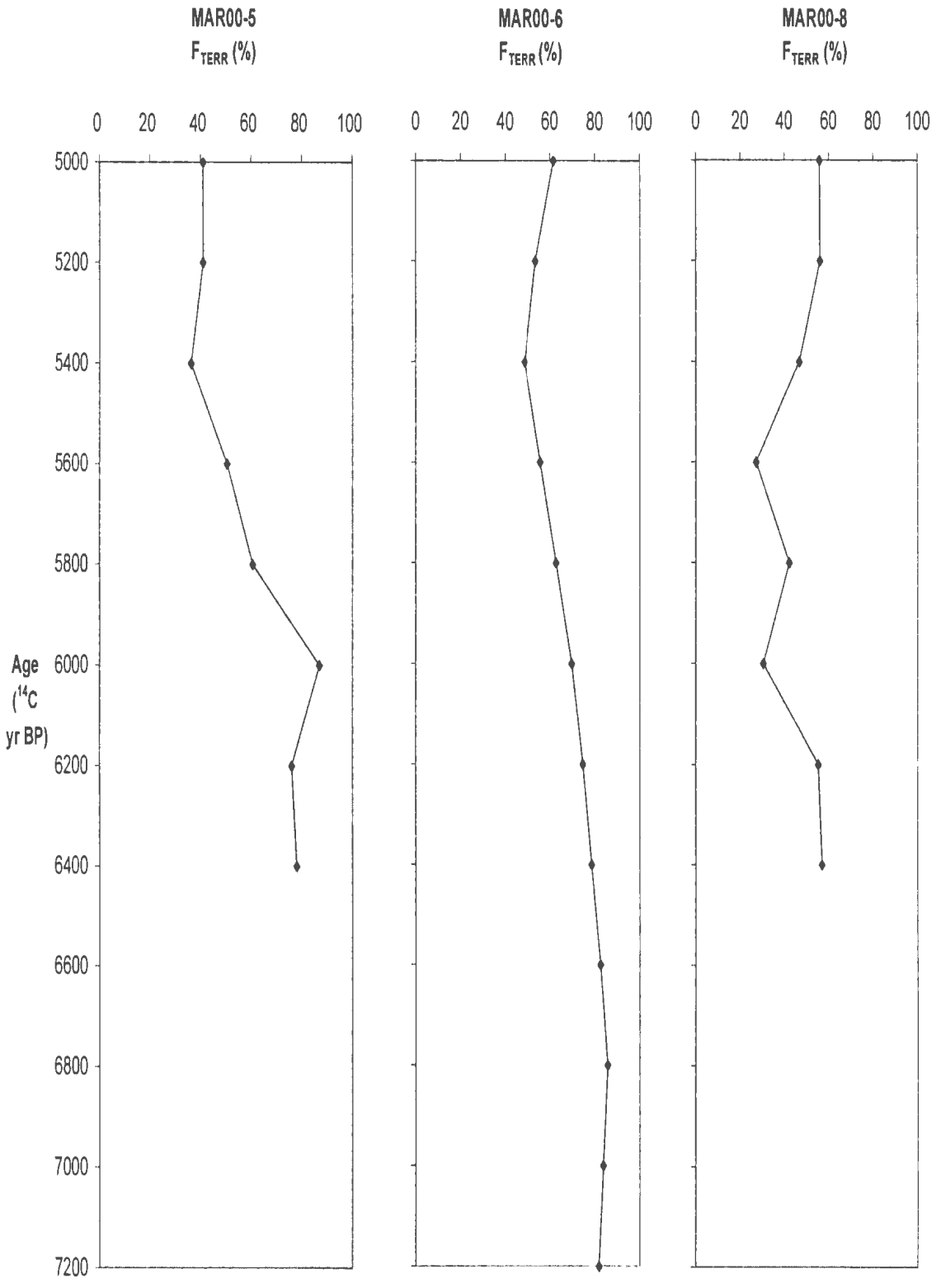


Figure 4.10 : Age Profiles (as uncalibrated conventional ^{14}C ages) of terrestrial organic carbon fraction (F_{TERR}) in the TOC for sediments older than ~5000 yr BP in Black Sea cores MAR00-5, MAR00-6 and MAR00-8

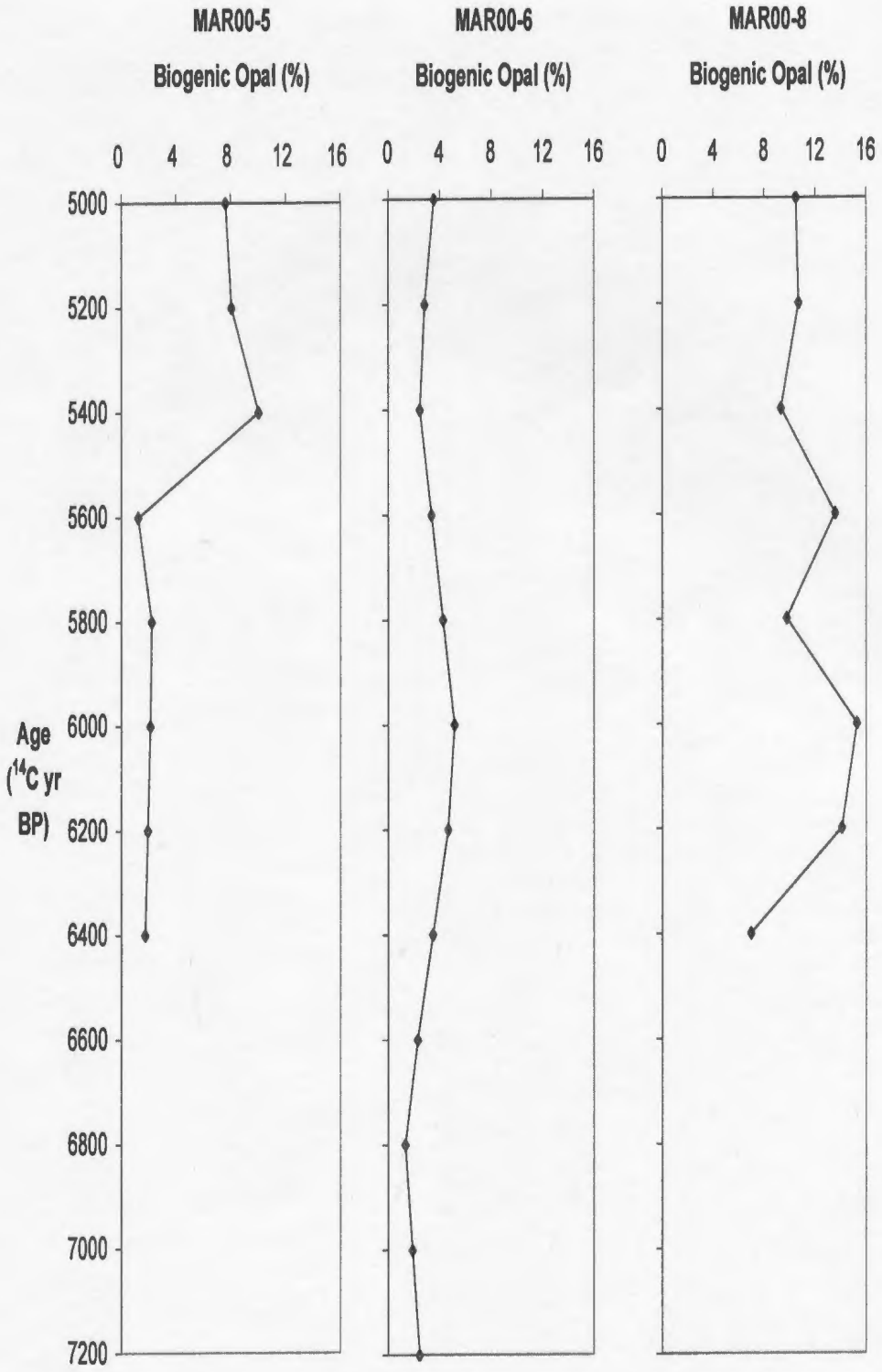


Figure 4.11 : Age Profiles (as uncalibrated conventional ^{14}C ages) of biogenic opal values for sediments older than ~5000 yr BP in Black Sea cores MAR00-5, MAR00-6 and MAR00-8

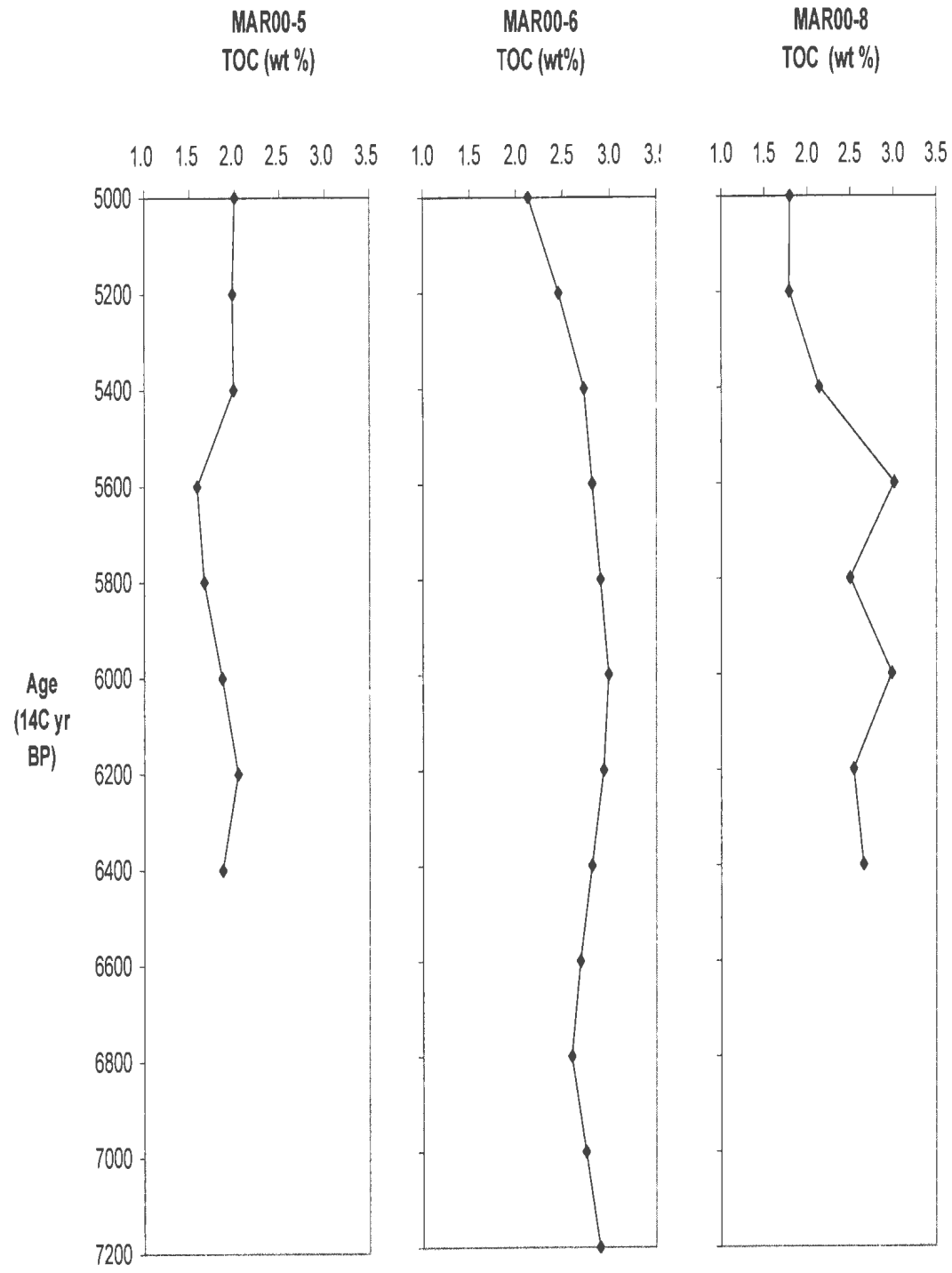


Figure 4.12 : Age Profiles (as uncalibrated conventional ^{14}C ages) of total organic carbon (TOC) values for sediments older than ~5000 yr BP in Black Sea cores MAR00-5, MAR00-6 and MAR00-8

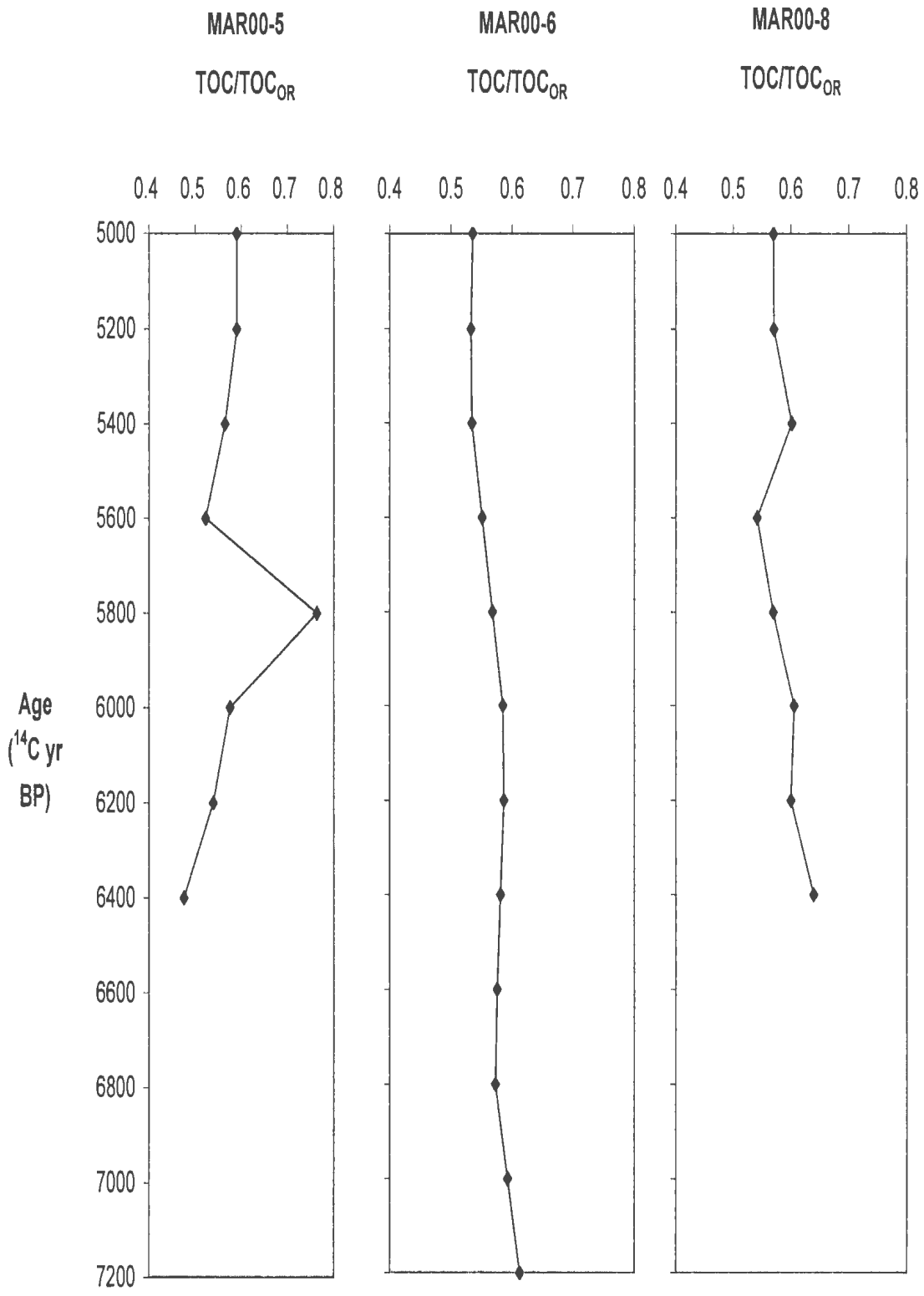


Figure 4.13 : Age Profiles (as uncalibrated conventional ^{14}C ages) of the degree of organic matter preservation (TOC/ TOC_{OR}) for sediments older than ~5000 yr BP in Black Sea cores MAR00-5, MAR00-6 and MAR00-8

organic matter. The greater susceptibility of core MAR00-5 sediments to diagenesis (which raises ^{3}C values) is also to be expected because the core site is at a shallower water depth, where burrowing and oxygenation would have been greater. An increased marine contribution to the TOC content of core MAR00-5 from ~5600 -5000 yr BP is shown by the relatively lower contribution of terrestrial organic carbon to the TOC (lower F_{TERR} values; Figure 4.10) coupled with increased biogenic opal content and more positive $\delta^{13}C$ values (Figures 4.11 and 4.9, respectively).

Concentrations of biogenic opal are generally higher (between 6 16%) in core MAR00-8 than in the other Black Sea cores (Figure 4.11). This can be attributed to an enhanced autochthonous contribution to the total organic pool from marine siliceous or organic-walled plankton as a result of increased marine primary productivity in the surface waters. This likely accounts for the elevated TOC content at this time (>2%). This interpretation is also consistent with $\delta^{13}C$ values between –24.3 to 25.27‰, and with a much lower fraction of terrestrial organic carbon (low F_{TERR}) from ~6400–5600 yr BP (Figure 4.10). However, the relatively small upcore decrease in TOC/TOC_{OR} (degree of organic carbon preservation; Figure 4.13) in this interval suggests that diagenesis has altered the carbon-isotopic composition and/or reduced the TOC content (as shown by the difference between the calculated initial organic carbon (TOC_{OR}) values (Figure 4.14) and the measured TOC content.

From 4800 yr BP in core MAR00-6, there is a general upcore decrease in F_{TERR} values (Figure 4.15), coupled with fluctuating increases in $\delta^{13}C$ and biogenic opal values. These data suggest a progressive upcore shift to more marine input, or an early predominance of C3 terrestrial plants, which commonly have $\delta^{13}C$ values of ~ 26‰. This

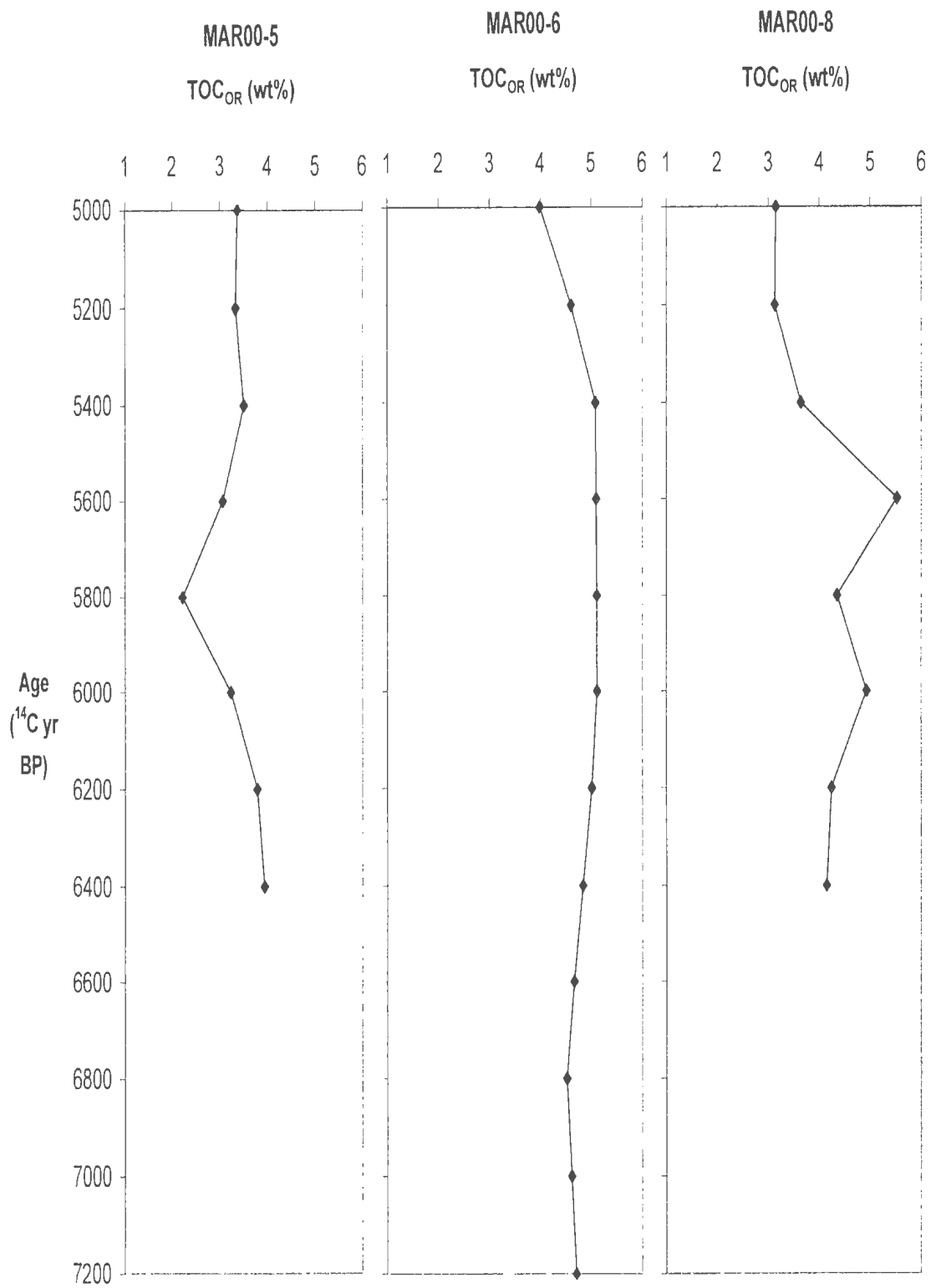


Figure 4.14: Age Profiles (as uncalibrated conventional ^{14}C ages) for calculated initial organic carbon values (TOC_{OR}) for sediments older than 5000 yr BP in Black Sea cores MAR00-5, MAR00-6 and MAR00-8.

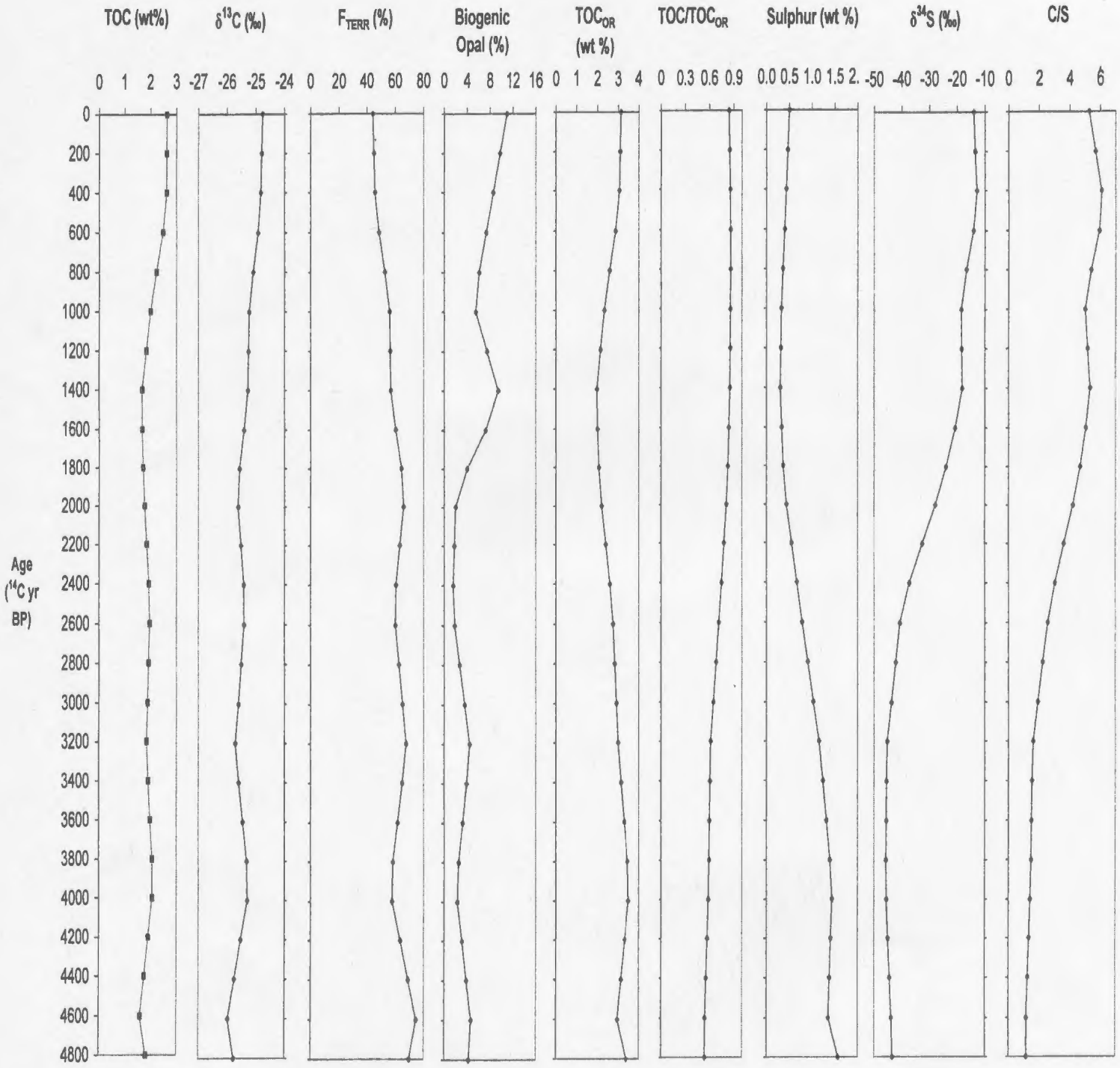


Figure 4.15: Age profiles (as uncalibrated conventional ^{14}C dates in yr BP) for key proxy variables TOC, $\delta^{13}C$, F_{TERR}, biogenic opal (silica), TOC_{OR}, TOC/TOC_{OR}, total sulphur, $\delta^{34}S$, and C/S in core MAR00-6 sediments younger than 5000 yr BP.

is particularly the case for sediments older than 1000 yr BP but younger than 4800 yr BP. The upcore decrease in the terrestrial organic-carbon fraction in this time interval further supports the hypothesis that there is an overall trend from terrestrial evolving to more marine contribution to the TOC. In the sapropel younger than 1000 yr BP, high TOC values coincide with relatively high biogenic opal and low F_{TERR} values. These data coupled with a high correlation between biogenic opal and TOC contents ($r = 0.885$; Figure 4.16) further support increased contribution from marine soureces even though the relatively lower $\delta^{13}C$ values appear somewhat terrestrial appear (mean = ~25).

4.3.2 Marmara Sea Core MAR98-11

In the Marmara Sea core MAR98-11, $\delta^{13}C$ values from ~12800 yr BP to the onset of, and throughout the deposition of sapropel from ~9800 to ~6600 yr BP (the latter corresponding to a core depth of ~180 cm) point to a predominantly terrestrial source for the organic matter (Figure 4.7; Table 4.4). This assessment is consistent with the higher fraction of terrigenous organic carbon (F_{TERR}) in this interval (Figure 4.7). The higher terrestrial input to the sapropel is attributed to organic-rich low-salinity outflow from the Black Sea that started ~10500-11000 yr BP. The Black Sea low-salinity surface water resulted in density stratification between it and the underlying marine water derived from the Aegean Sea. The higher salinity Aegean water entered the Marmara Sea when rising global sea level reached the Dardanelles sill at ~12000 yr BP. The observed trend to highest fraction of terrigenous organic carbon (F_{TERR}) at ~12000 yr BP then reverses; F_{TERR} decreases gradually towards the top of the sapropel at ~6600 yr BP (corresponding to a core depth of ~110 cm; Figure 4.7). This is similar to the distribution of marine and terrestrial organic carbon in contemporaneous sapropel S1 in the Aegean Sea (Aksu et al.,

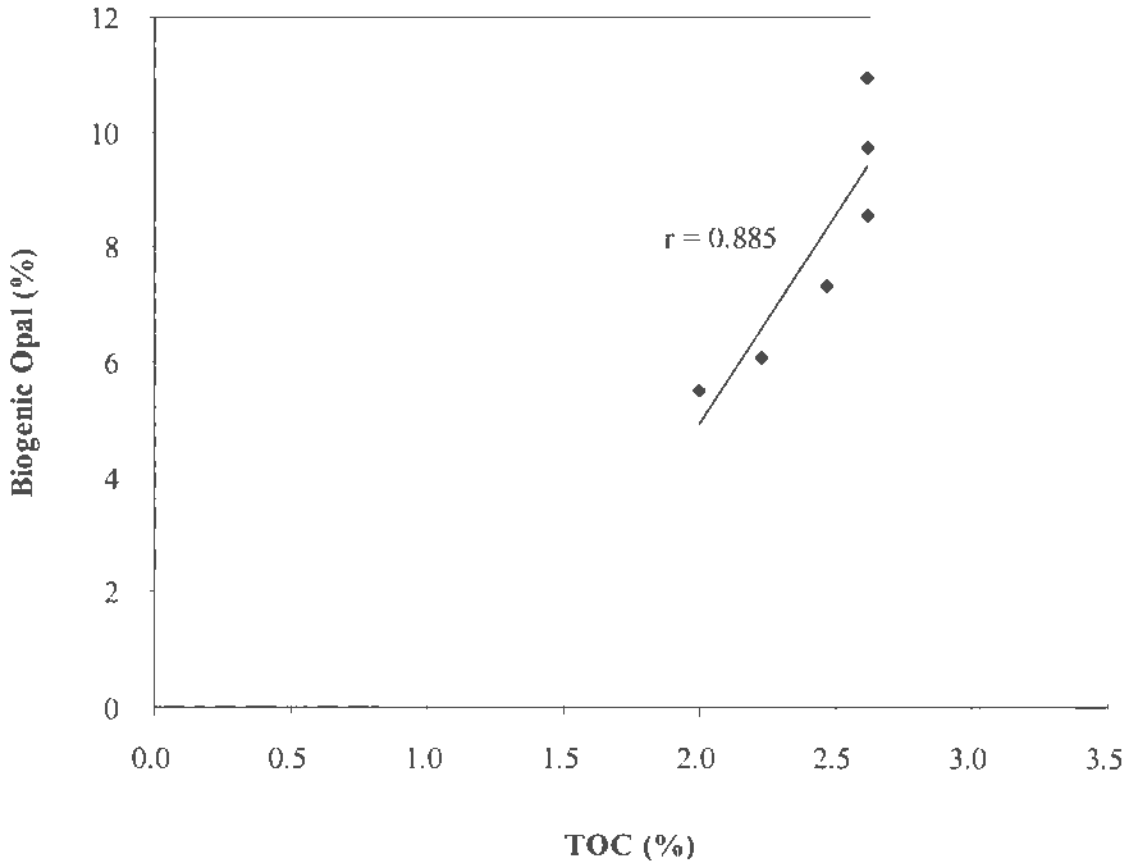


Figure 4.16: Cross plot of TOC (%) and biogenic opal (%) for the sapropel younger than 1000 yr BP in core MAR00-6. The Pearson Correlation coefficient, r is 0.885.

1995a, b). Abrajano et al. (2002) and Tolun et al. (2002) also recognized a high contribution of terrestrial organic carbon at the onset of sapropel M1 deposition in the Marmara Sea, decreasing towards the top of the sapropel, and attributed this to low-salinity input from river water entering the Black Sea and carrying terrestrial organic carbon.

The biogenic opal values in core MAR98-11 are relatively low to moderate compared to the Black Sea cores, and there is no correlation between TOC and biogenic opal content for the entire length of the core ($r = 0.049$; Figure 4.17). The lower biogenic opal values in Marmara Sea cores have been previously attributed by Abrajano et al. (2002) to a lower rate of photosynthetic fixation in the relatively "nutrient-poor" water-column of the Marmara Sea. From the base of the core at ~12800 yr BP to the onset of sapropel formation, there is a very weak negative correlation between TOC and biogenic opal ($r = -0.304$; Figure 4.18) while in the sapropel layer from ~9800 to ~6600 yr BP, there is an even weaker negative correlation between TOC and biogenic opal ($r = -0.158$; Figure 4.19). These negative correlations suggest that the factors that influence the distribution of opal and organic matter in this layer are different. The decoupling between biogenic opal and TOC in the ~9800 to ~6600 yr BP organic-carbon-rich laminated interval provides supportive evidence for enhanced preservation rather than increased or enhanced primary productivity to explain the elevated TOC. This enhanced preservation has previously been attributed to poor water-column ventilation caused by outflow of brackish water from the Black Sea into the Sea of Marmara. This resulted in density stratification during the deposition of sapropel M1 in the Marmara Sea (Abrajano et al., 2002; Aksu et al., 2002a, b; Tolun et al., 2002).

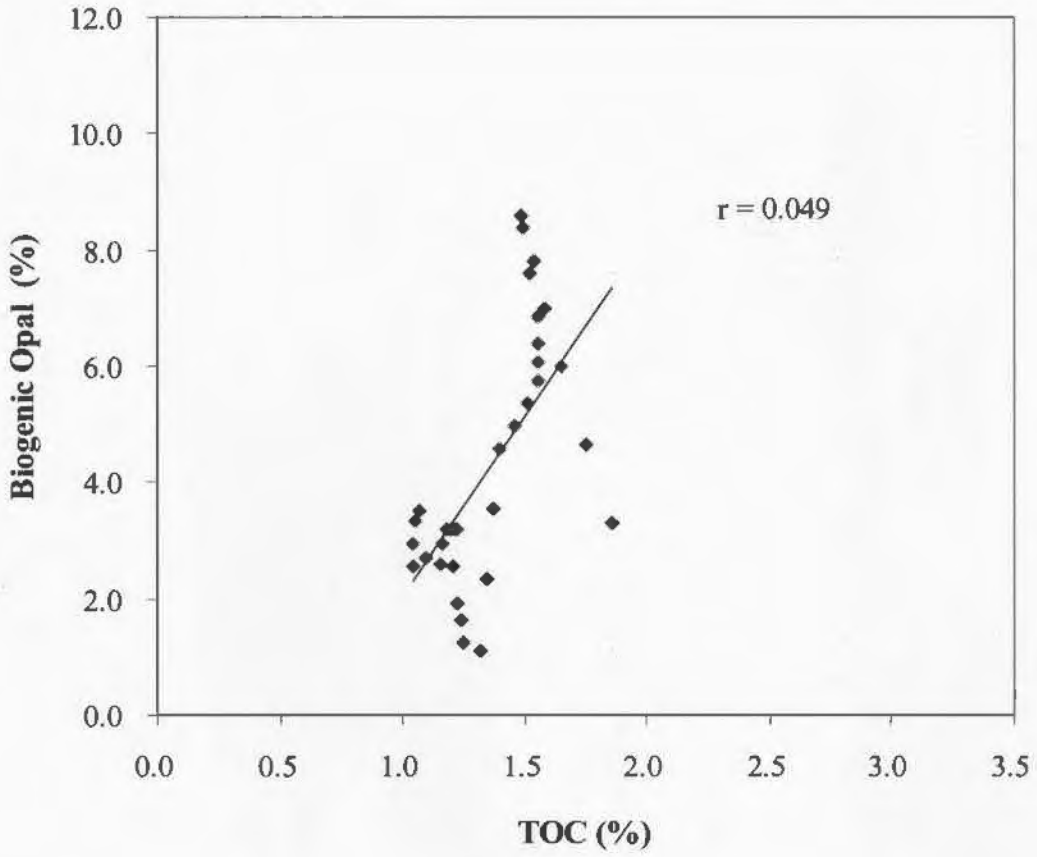


Figure 4.17: Cross plot of TOC (%) and biogenic opal (%) for core MAR98-11 sediments. The Pearson Correlation coefficient (r) is r= 0.049.

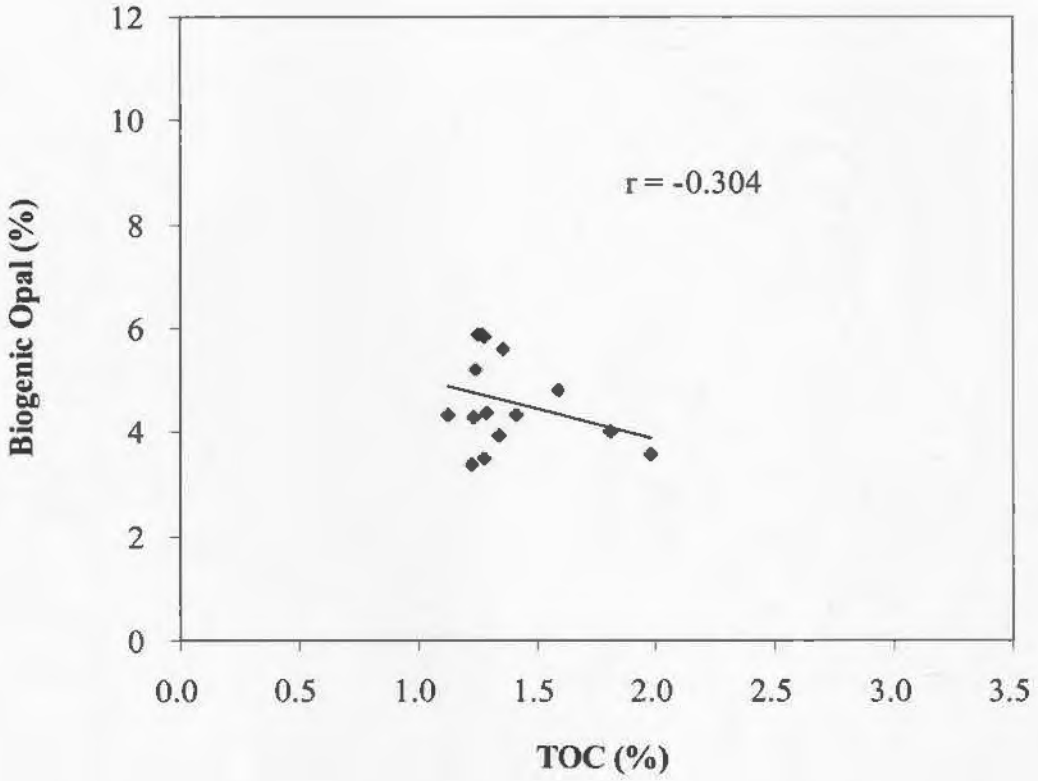


Figure 4.18: Cross plot of TOC (%) and biogenic opal (%) for sediments from ~12800 yr BP to ~10000 (prior to sapropel deposition) in core MAR98-11. The Pearson Correlation coefficient (r) is -0.304.

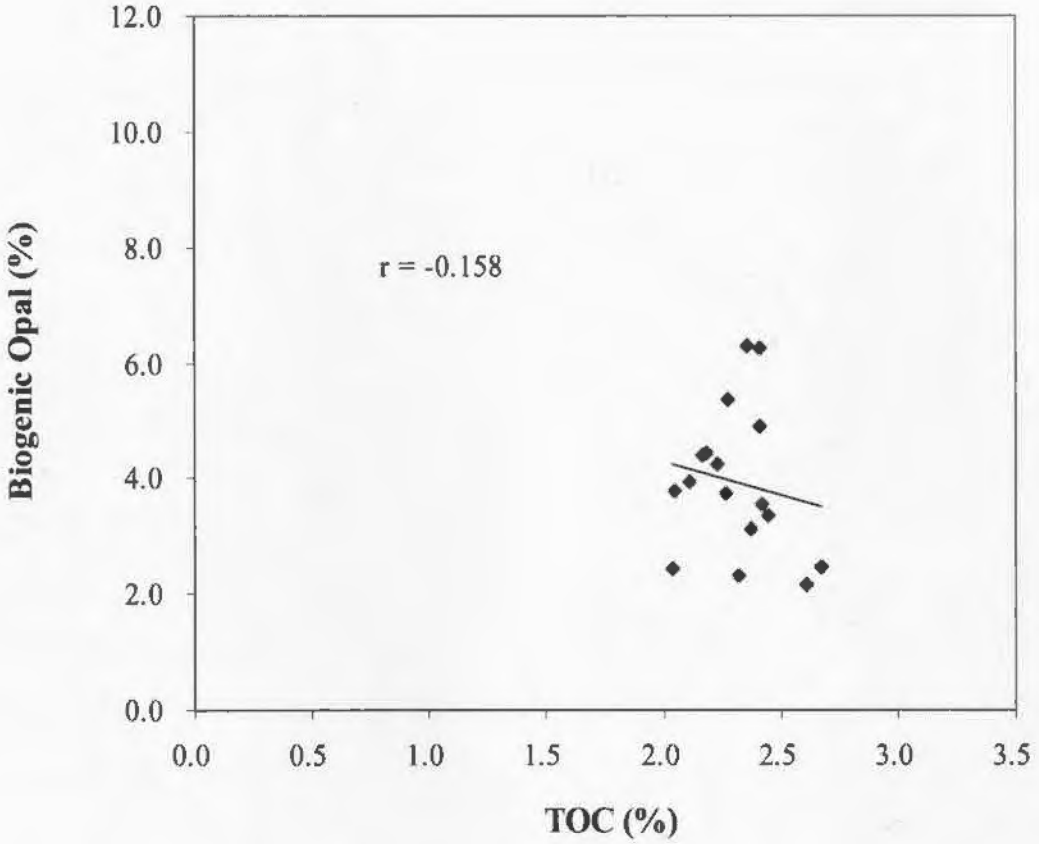


Figure 4.19: Cross plot of TOC (%) and biogenic opal (%) for sediments in the sapropel layer between ~9800 to ~6600 yr BP in core MAR98-11. The Pearson Correlation coefficient (r) is -0.158.

However, there is a significant positive correlation between biogenic opal and TOC ($r = 0.628$; Figure 4.20) in the sediments deposited from ~6400 yr BP to the top of the core (0-110 cm, Allounit A1; Figure 4.7), which points to an increasing contribution from marine sources in the surficial sediments. This is likely the result of increased marine primary production in the surface waters during this time interval. This assessment is supported by the subsequent significant decrease in terrigenous organic-carbon fraction of the TOC (and the corresponding increase in marine organic-carbon fraction; reflected in F_{TERR} values) and a trend towards relatively heavier marine carbon $\delta^{13}C$ signatures towards the top of the core (Figure 4.7; Table 4.4).

4.4 Depositional Environment and Bottom Water Conditions

The relationships between total organic carbon, reduced sulphur concentrations and bottom-water oxygen conditions during sedimentation have been widely studied and used as indicators of environmental conditions in bottom sediments. The basis of the technique lies in the process through which hydrogen sulphide, produced by sulphate reduction, reacts with iron oxide phases to form sedimentary pyrite. The extent of sulphate reduction and hence the amount of pyrite, is limited by the concentrations of deposited bacterially decomposable organic matter, the concentration of sulphate ions in the depositional waters and the availability of iron that can react with hydrogen sulphide to form sedimentary pyrite and its precursors (Berner 1984).

Berner and Raiswell (1984) and Raiswell and Berner (1985), among others, have used the weight percent ratio of the total organic carbon content to the total sulphur content (i.e. C/S ratio) of sediments to determine the level of oxygenation of the depositional environment, and to distinguish between non-marine (brackish, freshwater),

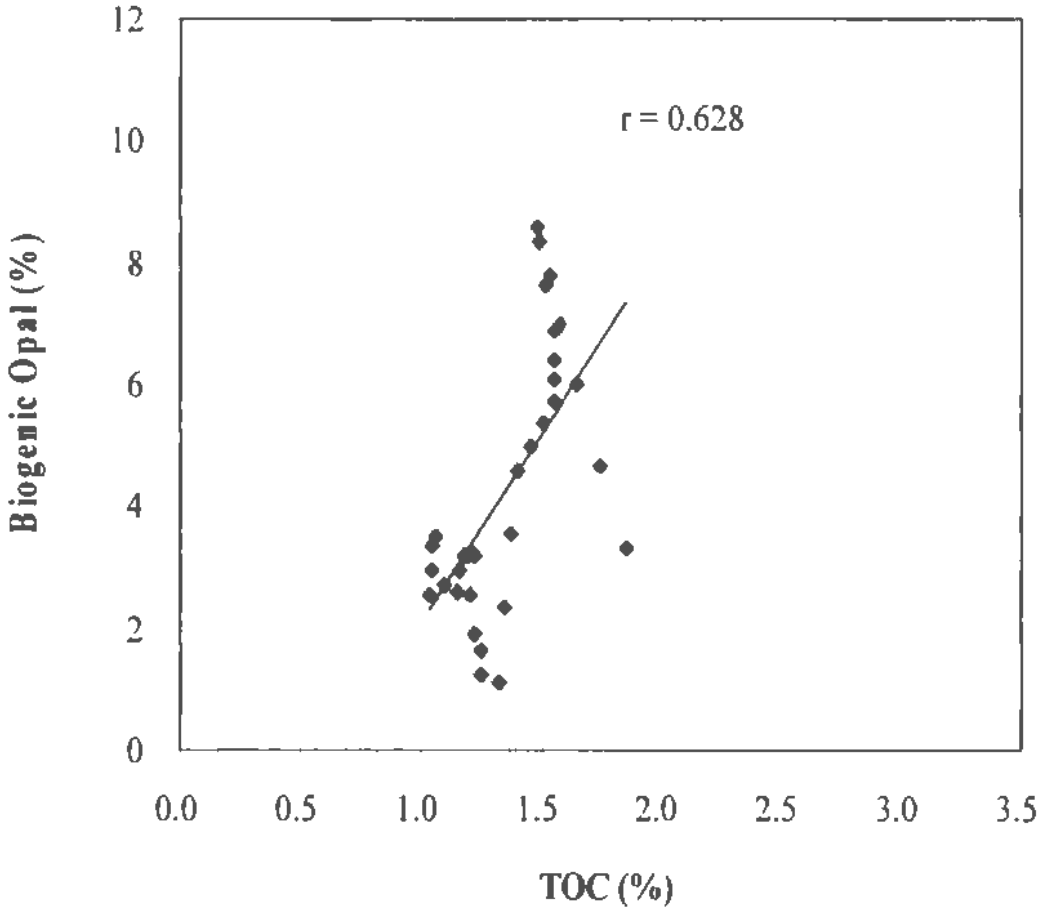


Figure 4.20: Cross plot of TOC (%) and biogenic opal (%) for sediments deposited from ~6400 yr BP to present in core MAR98-11. The Pearson Correlation coefficient (r) is 0.628.

aerobic and anaerobic marine, and euxinic (sulphidic bottom waters) depositional settings (Berner and Raiswell, 1984). The factors that determine the C/S ratios are (1) the fraction of organic carbon that is metabolized, (2) the fraction of metabolized organic carbon that is metabolized via sulphate reduction, and (3) the fraction of sulphide that is not oxidized and is buried as pyrite (Morse and Berner, 1995).

The well-established C/S ratios for Quaternary normal-marine sediments (i.e. sediments deposited under an oxic water column) are 2.8 ± 0.8 (Berner 1984; Raiswell and Berner 1986). According to Leventhal (1983) and Berner (1989) C/S ratios lower than 2.8 are indicative of sediments with a trend to anoxic conditions. Typical ranges of C/S ratios for various depositional environments (conditions) are given in Table 4.7.

Similarly, TOC versus total sulphur cross plots have also been used to show changes, which are indicative of variations in the salinity of the paleoenvironment (Berner and Raiswell, 1984; Lyons and Berner, 1992; Figure 4.21), and to provide information on diagenetic processes (Berner, 1984; Canfield, 1989; Canfield et al., 1992; Lyons and Berner, 1992; Raiswell and Canfield, 1998).

In the TOC versus total sulphur cross plots, the weight percentage of total organic carbon (TOC), a reasonably accurate measure of total organic matter, is plotted against percentage of pyrite sulphur, measured as the weight percentage of the total sulphur content (TS) for normal marine sediments, to yield positive linear trends, with the regression line passing through the origin (Berner 1970, 1982; Berner and Raiswell 1983; Figure 4.21). This positive linear trend results because pyrite formation is organic carbon limited and the sediment behaves as though a constant proportion of the organic matter originally deposited is degraded. The residual portion of the organic matter (which cannot

Depositional Environments (conditions)	C/S Values
Freshwater	>10
Oxic marine	2.8 ± 1.8
Brackish sediments	3-6

Table 4.7: Typical ranges of C/S ratios for various depositional environments (conditions). Berner and Raiswell 1983

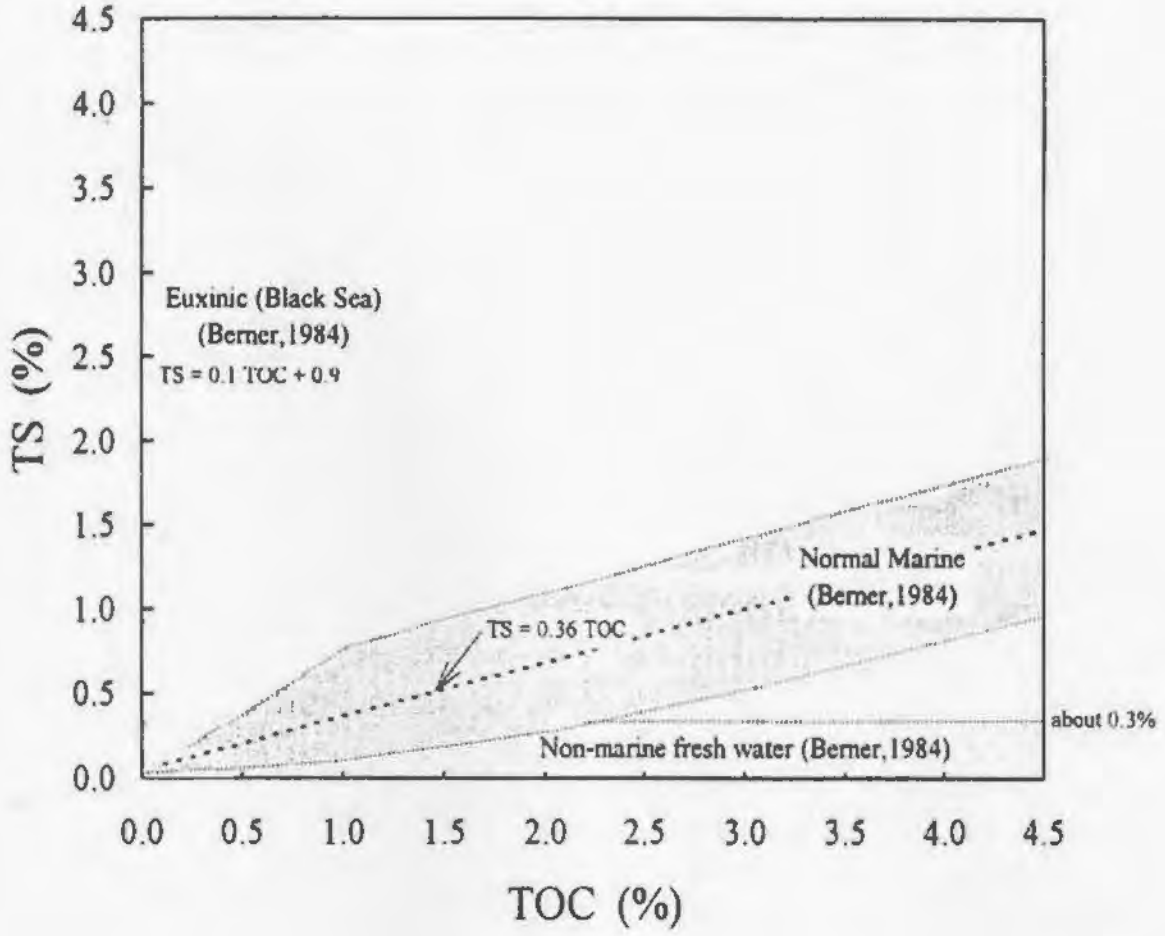


Figure 4.21: TOC-total sulphur (TS) cross plot showing the normal marine regression line of Lyons and Berner (1992) used as an indicator of environmental conditions (oxygenation) in bottom sediments and to distinguish the variations in the degree of salinity of the depositional environment by Berner (1984). The shaded area in the plot represents the envelope where sediments deposited under oxic-suboxic conditions usually plot. Diagram was modified from Sampei et al. (1997; their figure 7).

cannot be metabolized) correlates with the amount of pyrite formed.

Figure 4.21 gives a mean value of 2.8 for the C/S ratio for modern and ancient normal marine sediments (those deposited from oxygenated bottom waters) and a regression line passing through the origin. Freshwater sediments typically plot well below this normal marine regression line. Sediments deposited under brackish conditions plot much closer to the normal marine regression line than freshwater sediments. Sediments from euxinic (anoxic) marine environments like the Black Sea have very low C/S ratios because the abundant sulphate in seawater is reduced to H_2S. These sediments plot above the normal marine regression line.

In this thesis, the C/S ratios were estimated by dividing the total organic carbon content (in weight percent) by the weight percent of the total sulphur (in weight percent), assuming that the total sulphur content reflects pyrite in the sediments.

4.4.1 Black Sea Cores

The relatively high total sulphur content (higher than 0.3%, the reported value for non-marine freshwater sediments; Berner and Raiswell, 1983) and C/S ratios generally <2 (Figure 4.22) suggests predominantly marine depositional conditions before 5000 yr BP in the Black Sea (i.e. deposition under oxygenated water conditions; Berner and Raiswell, 1983). There is however, a spike to 3.54 in the C/S ratio and a concomitant decrease in total sulphur content at 5800 yr BP in core MAR00-5 (Figure 4.23) which likely indicates changing environmental conditions towards less saline conditions. Further support for marine depositional conditions is given by the presence of bivalve shells and shell-rich layers that contain fauna of marine affinity represented notably by Mytilus spp. and Cardium spp. These are burrowing invertebrates that can withstand low

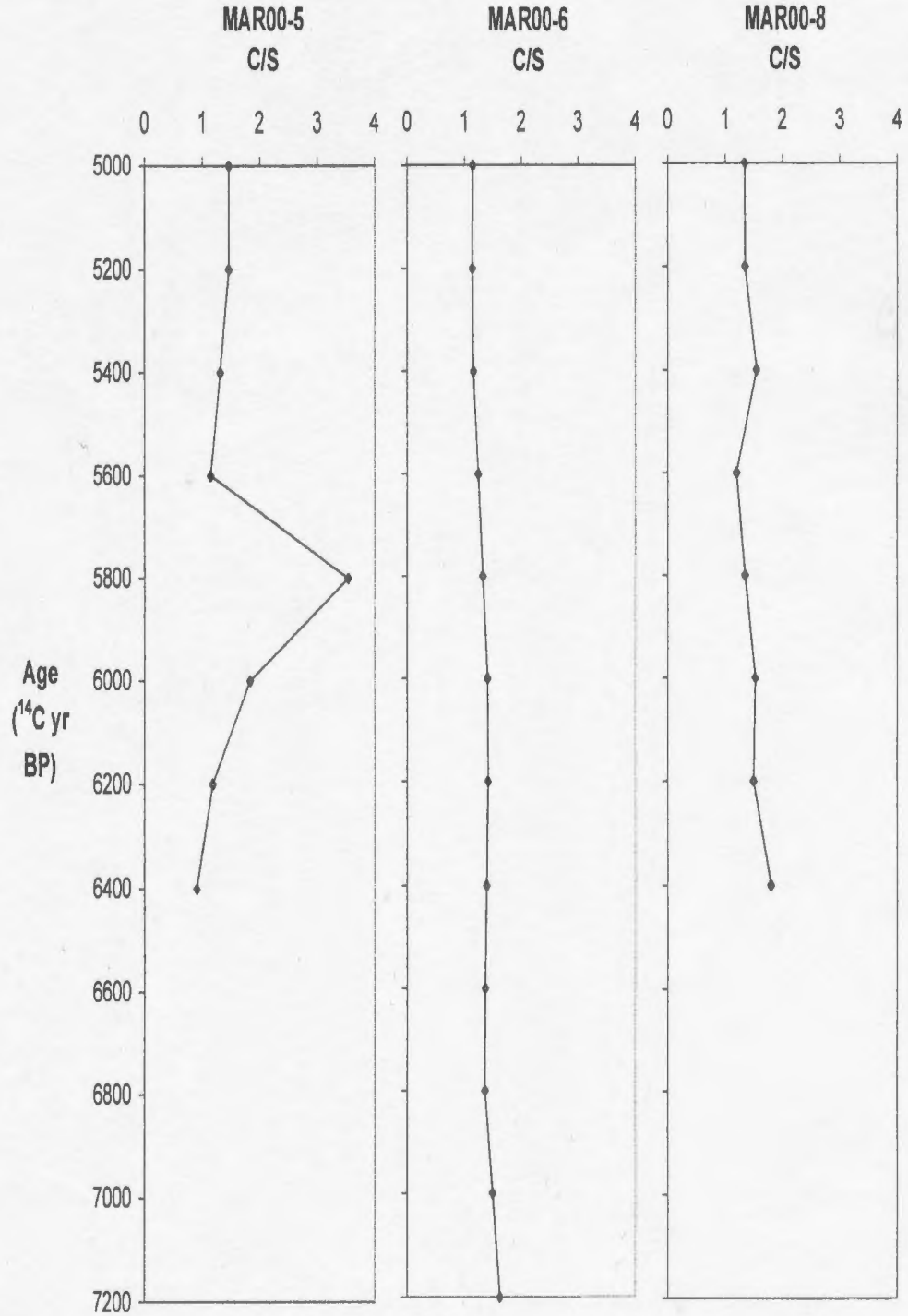


Figure 4.22: C/S ratios for sediments older than 5000 yr BP in the Black Sea cores MAR00-5, MAR00-6 and MAR00-8.

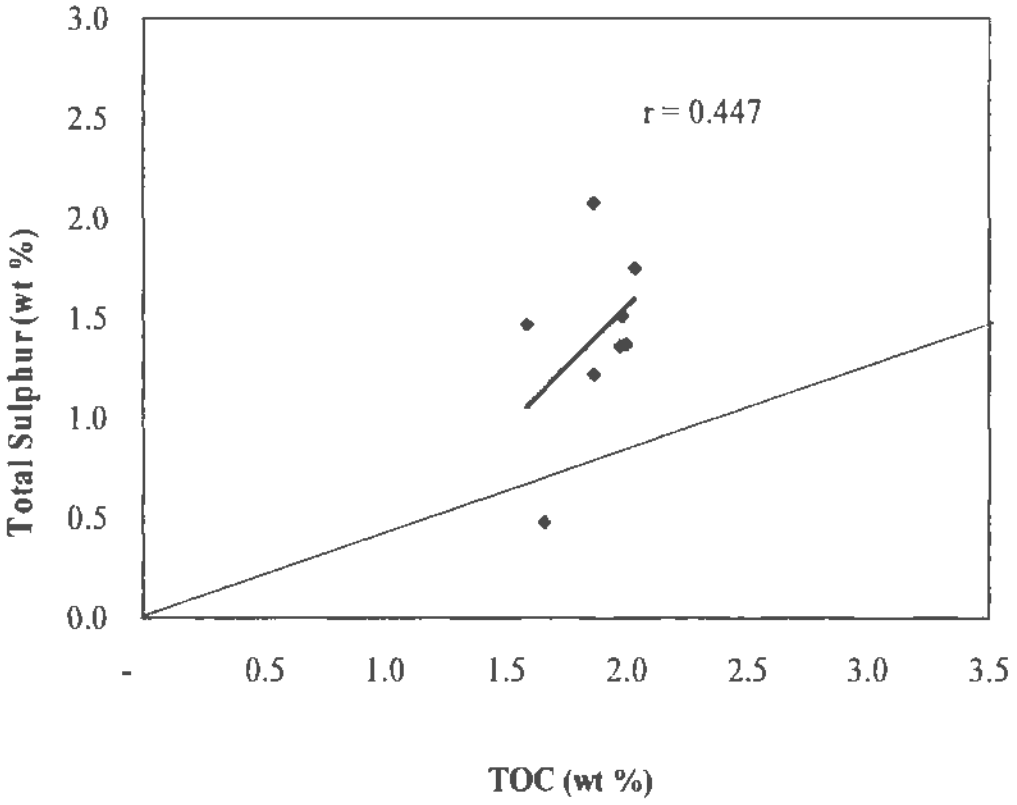


Figure 4.23: Cross plot of TOC (%) and total sulphur (%) for the Black Sea core MAR00-5. The Pearson correlation coefficient (r) = 0.447. The line that passes through the origin is the normal marine regression line of Lyons and Berner (1992) and Berner and Raiswell (1984, 1985).

oxygen conditions. While both taxa are found in core MAR00-5, only the latter is found in both cores MAR006 and MAR00-8 (Aksu et al, 2002b, their Table 2). In core MAR00-5, Mytilus spp. are found from 0-60 cm in sediments younger than 5460 yr BP, and Cardium spp. are found below 167 cm in sediments older than 6600 yr BP. The shell-rich layers and scattered shells in the Black Sea cores point to a shallow, benthic, marine setting influenced by waves and currents.

The C/S ratios in the Black Sea cores are relatively much lower than those than those observed in normal marine sediments (2.8 ± 0.8; Berner and Raiswell, 1983). This is likely due to carbon loss during burial, promoted by bioturbation and suggested in the cores by the presence of moderate burrows density. Irrigation of the sediments by the burrowing organisms also likely enhanced sulphate reduction by facilitating sulphate diffusion into the sediments from the overlying sulphate-rich (marine) waters. Reduced levels of oxygen in the bottom waters may have also enhanced sulphate reduction. The low C/S ratios are a further indication of higher water salinities and oxygenation in the water column, indicating deposition in a normal marine environment.

There are significant variations in the TOC-TS plots in the Black Sea cores. For sediments older than 5000 yr BP in the three cores (Figures 4.24, 4.25 and 4.26 for cores MAR00-5, MAR00-6 and MAR00-8, respectively), all samples plot above the regression line for normal marine sediments suggested by Berner and Raiswell (1984). However, most of the samples in cores MAR00-5 and MAR00-8 (Figures 4.25 and 4.27, respectively) cluster within the oxic-suboxic field (shaded area in Figure 4.23) than core MAR00-6 that plots in the euxinic zone (well above the normal marine regression line; Figure 4.27a).

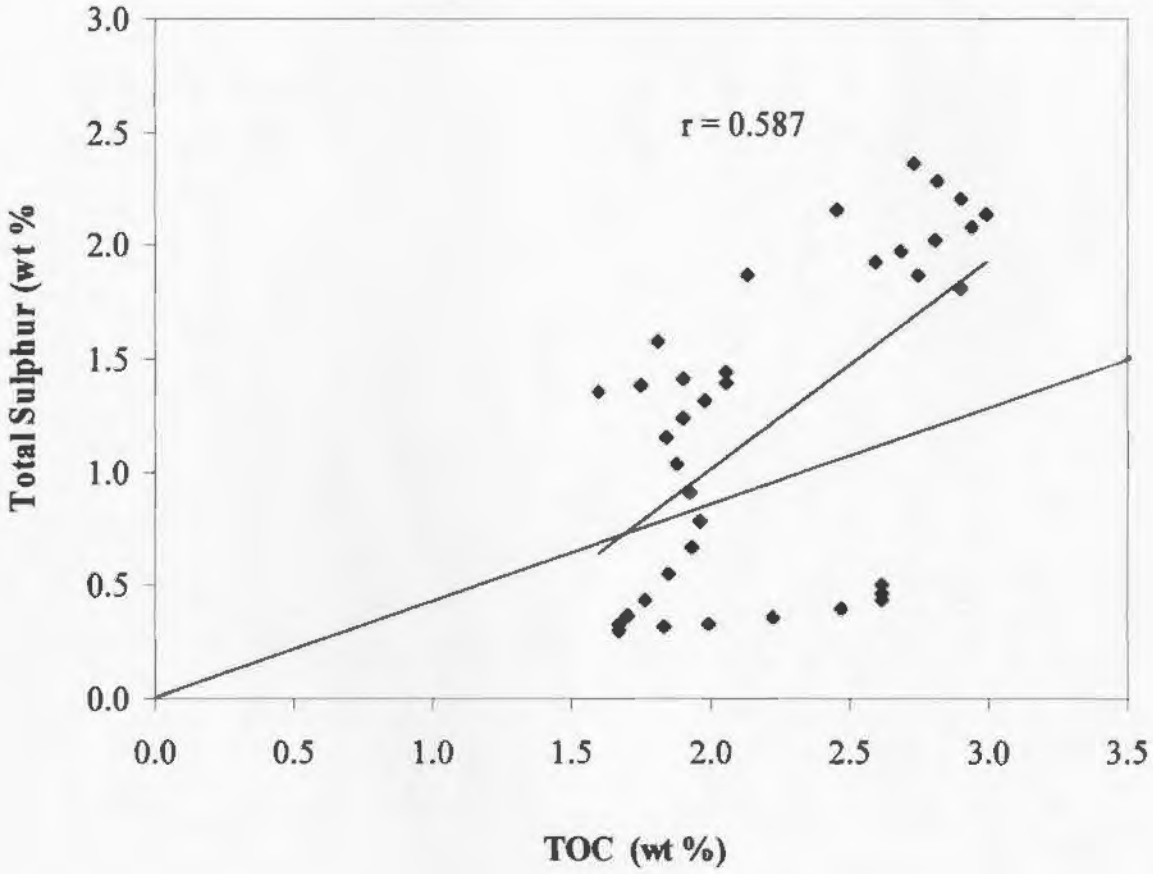


Figure 4.24: Cross plot of TOC (%) and total sulphur (%) for the Black Sea core MAR00-6. The Pearson correlation coefficient (r) = 0.587. The line that passes through the origin is the normal marine regression line of Lyons and Berner (1992) and Berner and Raiswell (1984, 1985).

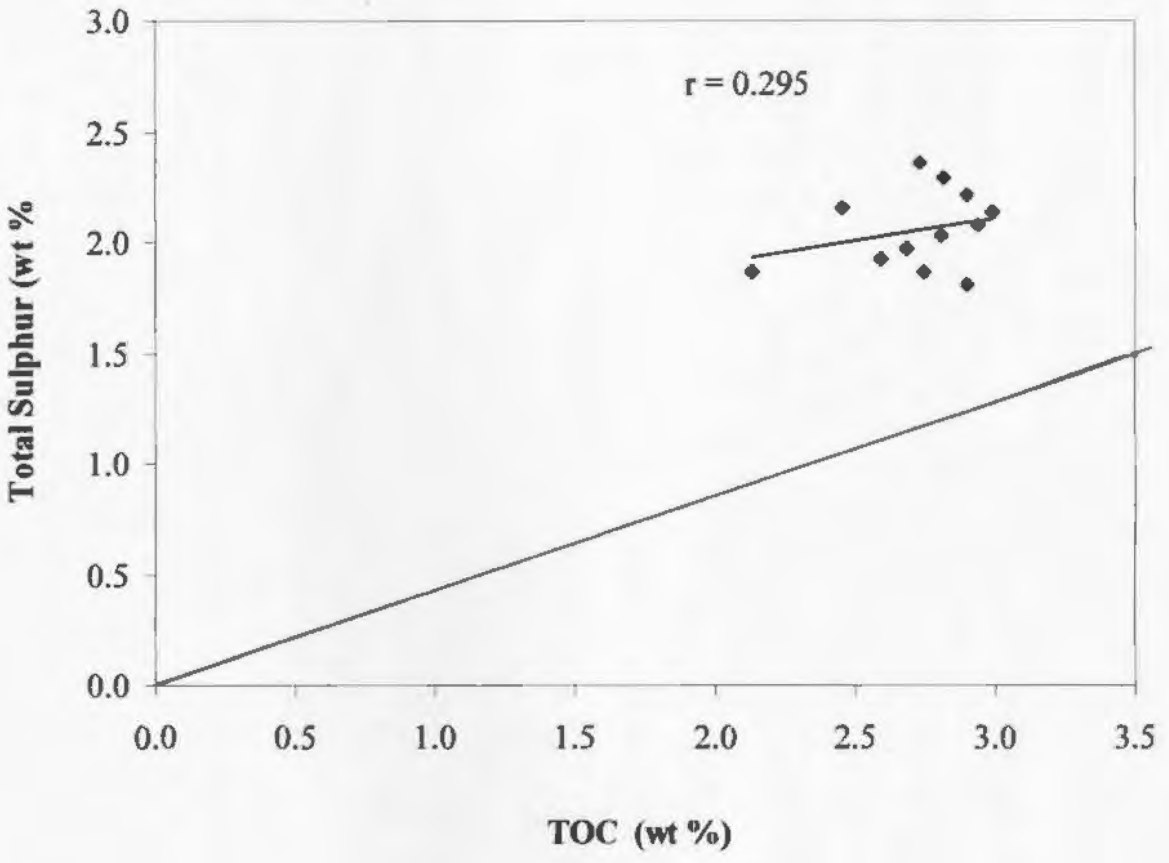


Figure 4.25: Cross plot of TOC (%) and total sulphur (%) for sediments older than 5000 yr BP in the Black Sea core MAR00-6. The Pearson correlation coefficient (r) = 0.295. The line that passes through the origin is the normal marine regression line of Lyons and Berner (1992) and Berner and Raiswell (1984, 1985).

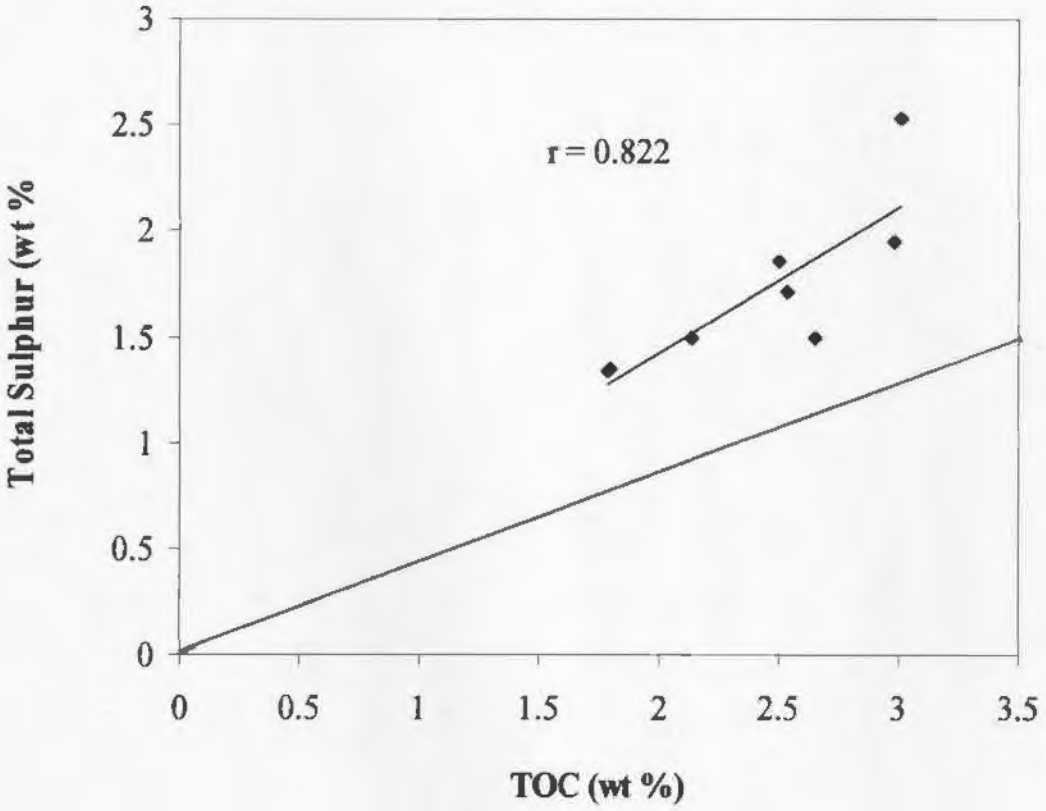
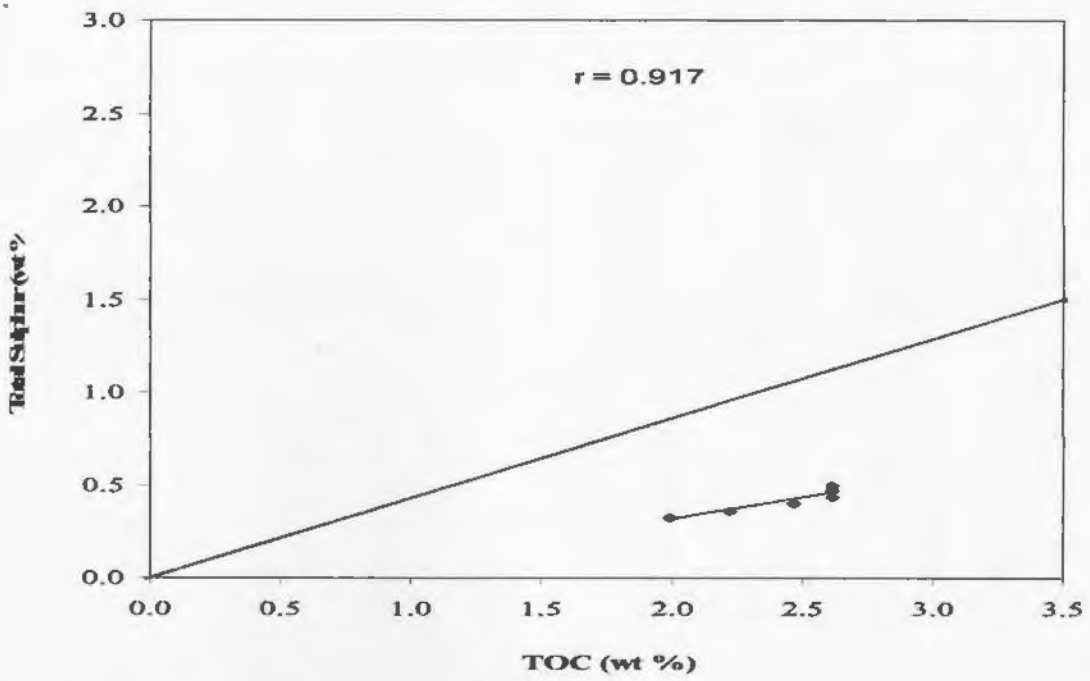
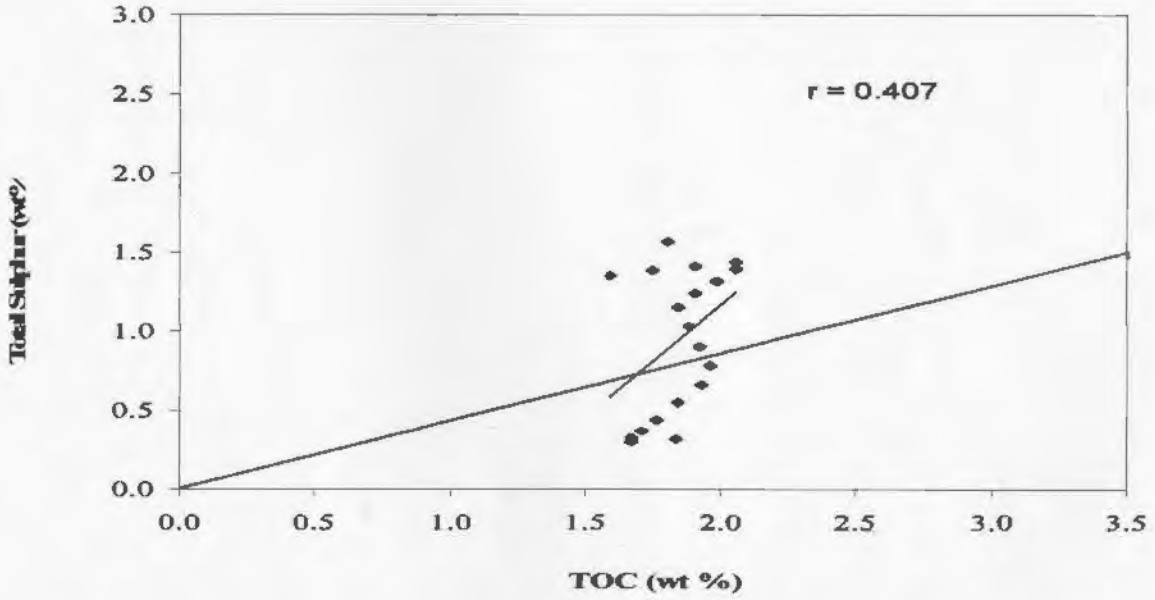


Figure 4.26: Cross plot of TOC (%) and total sulphur (%) for the Black Sea core MAR00-8. The Pearson correlation coefficient (r) = 0.822. The line that passes through the origin is the normal marine regression line of Lyons and Berner (1992) and Berner and Raiswell (1984, 1985).



(a) Sediments younger than 1000 yr BP. Pearson correlation coefficient (r) = 0.917



(b) Sediments older than 1000 yr BP but younger than 5000 yr BP. Pearson correlation coefficient (r) = 0.407.

Figures 4.27: Cross plot of TOC (%) and total sulphur (%) for core MAR00-6 sediments (a) younger than 1000 yr BP and (b) deposited between 1200-4800 yr BP. The line that passes through the origin is the normal marine regression line of Lyons and Berner (1992) and Berner and Raiswell (1984, 1985).

For sediments younger than 5000 yr BP in core MAR00-6, particularly in sediments younger than 2600 yr BP, there is a significant upcore increase in $\delta^{34}S$ to notably more positive values (Figure 4.15) as well as a decrease in total sulphur content to values near the 0.30% reported for non-marine freshwater sediments (Berner and Raiswell, 1983). These data indicate varying environmental conditions in a sulphate-poor depositional environment (Berner, 1981). This was not a normal open-marine setting, because of partial isolation from the world ocean. This interpretation is supported by C/S ratios between 2 and 6 (Figure 4.22), which are characteristic of brackish/brackish-marine environments. The color-banded greenish-gray and black muds that characterize this time interval suggest that oxygen levels were low and that conditions were reducing, accounting for the lack of bioturbation and shells in the sediments. The trend towards lighter $\delta^{34}S$ values in the 4800-1200 yr BP sediments most likely represents ^{34}S-depleted sulphate originally from a marine source, corroborated by C/S ratios that are predominantly <2.

The strongly enriched $\delta^{34}S$ values, the relatively low total sulphur content and C/S ratios between 5 and 6 (Figure 4.22) in the TOC-rich intervals younger than 1200 yr most likely reflect generally non-sulphidic, suhoxic conditions which are consistent with TOC-rich sediments deposited under iron-limited dysoxic and/or anoxic conditions.

TOC-TS cross plots for the TOC-rich sediments younger than 1000 yr BP and for older sediments younger than 4800 yr BP are shown in Figures 4.27a and Figures 4.27b, respectively. While the TOC-rich sediments plot in the non-marine field below the normal marine regression line of Figure 4.21, the sediments deposited between 4800-

1200 yr BP show more scatter, and generally plot in the zone of oxic deposition (shaded area in Figure 4.21).

These results lead to the conclusion that sediments younger than 5000 yr BP in core MAR00-6 were deposited in a restricted environment with some brackish influence in which there was a reduction in oxygen content of the bottom waters. Throughout this period, the MAR00-6 core site probably experienced variable reducing conditions from suboxic, to reducing, and then to anoxic (sulphate reducing).

4.4.2 Marmara Sea Core MAR98-11

Considerable scatter in the TOC-TS cross plot for core MAR98-11 (Figure 4.28) is probably the result of variations in total sulphur content and variability in depositional conditions. Sediments can be grouped into three categories based on how they plot on the TOC-TS plot. (1) Sediments older than 10000 yr BP plot near the normal marine regression line (Figure 4.29b) and have C/S ratios similar to sediments deposited under oxygenated bottom water conditions (i.e. less than or equal to 2.88). (2) The 9800-6600 yr BP sapropel M1 plots as a non-linear loop (Figure 4.29a). (3) Sediments younger than 6400 yr BP plot in the non-marine field of the TOC-TS plot (below the normal marine regression line) and have C/S ratios that are consistent with non-marine sediments (Figure 4.30). This third group of sediments can be further separated into those older than 4200 yr BP which have C/S ratios between 3 and 6 characteristic of brackish and/or brackish-marine conditions, and sediments younger than 4200 yr BP which are characterized by relatively high C/S ratios (>7), very low but constant total sulphur values and upward decreasing TOC content. The latter C/S, total sulphur and TOC data are indicative of sulphate-depleted pool typical of freshwater to moderately brackish

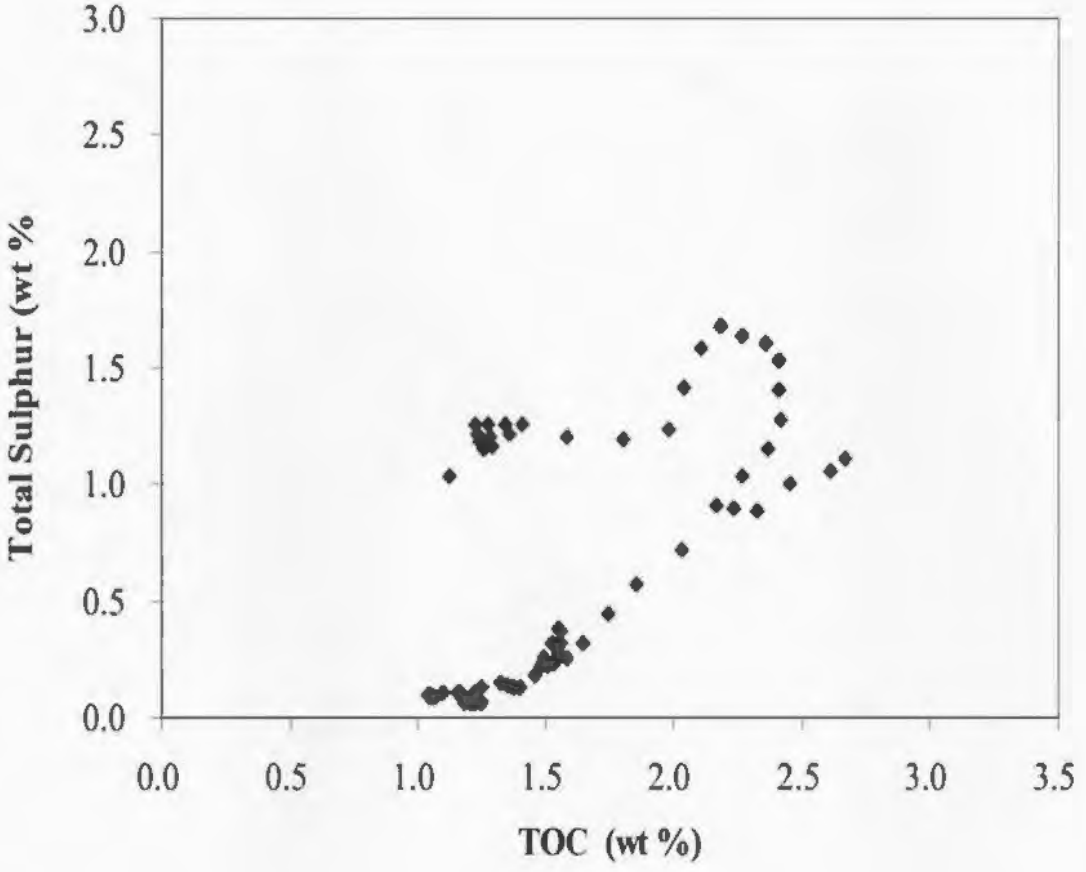
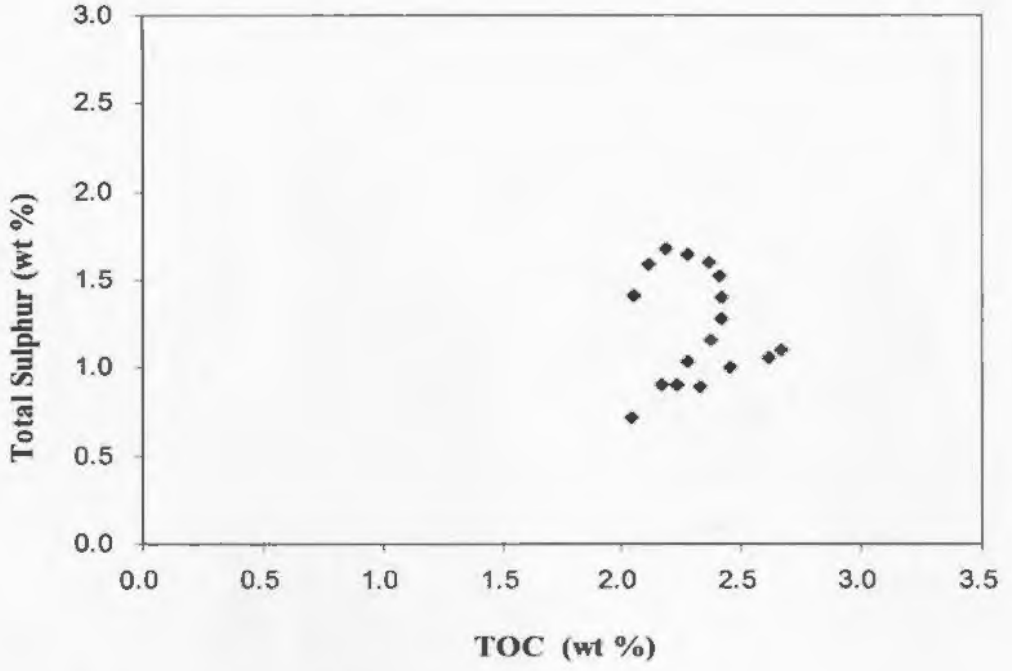
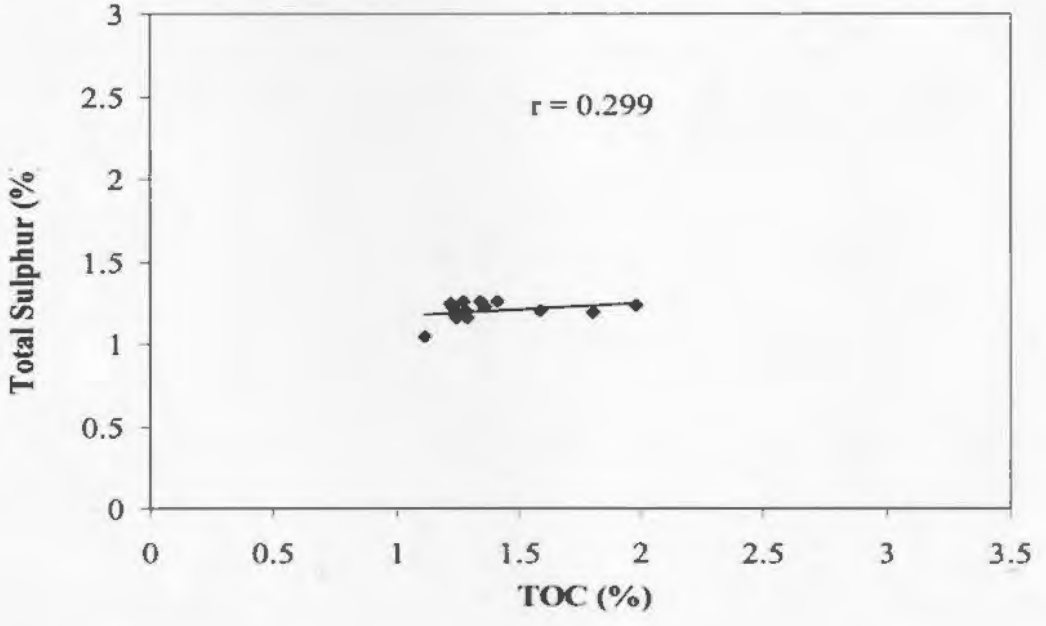


Figure 4.28: Cross plot of TOC (%) and total sulphur (%) for all sediments in the Marmara Sea core MAR98-11. The line that passes through the origin is the normal marine regression line of Lyons and Berner (1992) and Berner and Raiswell (1984, 1985).



(a) Sapropel sediments from 9800-6600 yr BP.



(b) Sediments deposited prior to sapropel deposition from 12800-10000 yr BP. Pearson correlation coefficient (r) = 0.299.

Figure 4.29: Cross plot of TOC (%) and total sulphur (%) for Marmara Sea core MAR98-11 (a) sapropel sediments from 9800-6600 yr BP and (b) sediments deposited prior to sapropel deposition from 12800-10000 yr BP. The line that passes through the origin is the normal marine regression line of Lyons and Berner (1992) and Berner and Raiswell (1984, 1985).

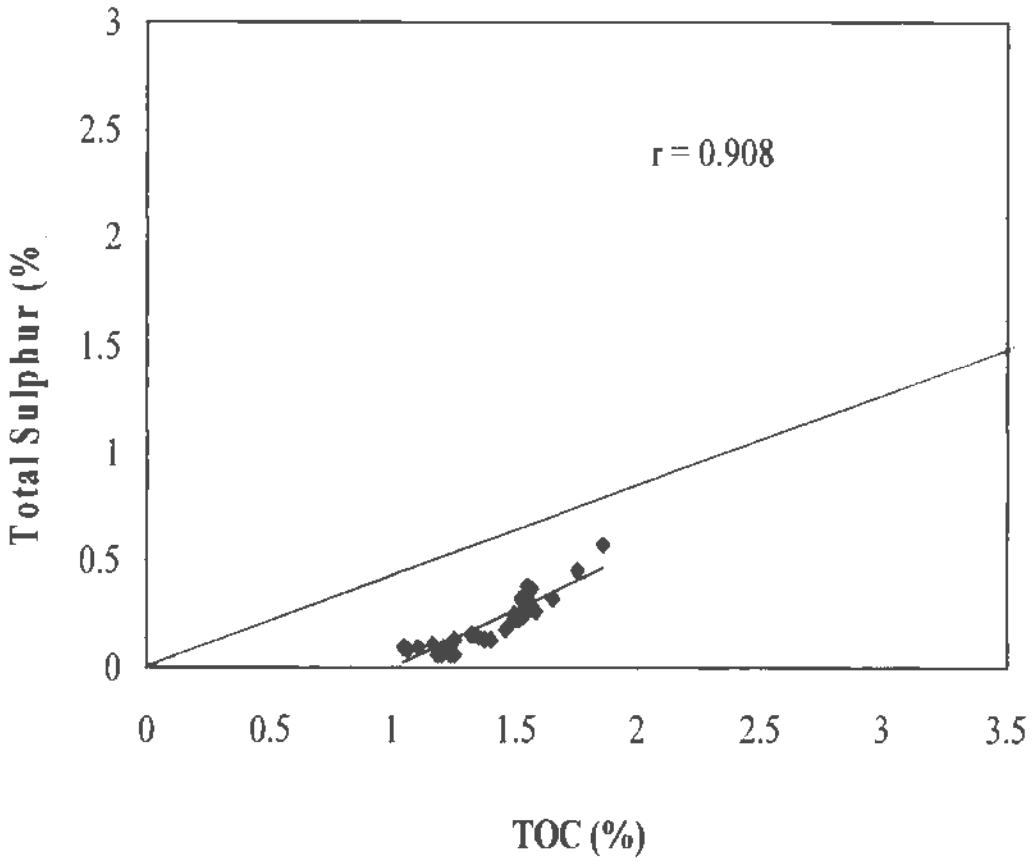


Figure 4.30: Cross plot of TOC (%) and total sulphur (%) for core MAR98-11 sediments younger than 6400 yr BP. The Pearson correlation coefficient (r) = 0.537. The line that passes through the origin is the normal marine regression line of Lyons and Berner (1992) and Berner and Raiswell (1984, 1985).

depositional environments (Berner and Raiswell, 1984).

However, because the relatively high C/S ratios in the sediments younger than 4200 yr BP reflect their low sulphur contents, the environment was more likely a low-salinity marine environment (moderately brackish with a generally lower sulphur content) rather than a freshwater environment. C/S ratios in the TOC-rich (sapropel) sediments in core MAR98-11 are typical of marine sediments, accounting for the fact that they plot in the oxic depositional field of the TOCC-TS plot (shaded area in Figure 4.21). Low-oxygen and/or anoxic bottom water conditions in the sapropel can also be further supported by the presence of mm-scale laminations accentuated by color banding, and the relative upcore decrease in $\delta^{34}S$ values with the attendant increase in TOC content in the sediments (compared to the rest of the core).

4.5 Organic Carbon Degradation and Preservation

According to Müller et al. (1988), the quantity of preserved organic carbon in sediments depends on the organic matter supply from the surface layer of the ocean, water depth, bulk sedimentation rate, and any oxidation of the carbon supply by bottom water oxygen and other oxidants. In marine sediments, organic carbon is usually oxidized aerobically to a depth of 1-2 cm beneath the sediment surface and degraded anaerobically below this depth (Canfield and Berner, 1987). Aerobic organic carbon oxidation is relatively fast and efficient, while the anaerobic process usually involves bacterially mediated reduction of sulphate and production of hydrogen sulphide. Furthermore, it has been generally accepted that aerobic respiration and sulphate reduction each account for up to half of the total organic carbon oxidation in marine sediments underlying an oxic water column (Jørgensen, 1983), while sulphate reduction is the dominating process for

organic carbon oxidation in sediments underlying an oxygen-deficient water column (Thamdrup and Canfield, 1996). The two degradation pathways and the effects of their interactions have a great influence on the burial and preservation of organic carbon in the sediments.

However, there is an ongoing debate about the effect of oxygen concentration on organic carbon degradation (i.e. differences between aerobic and anaerobic processes). Several studies (e.g. Kristensen and Holmer, 2001) have argued that, for highly degradable organic matter, aerobic and anaerobic degradation rates are similar, whereas the aerobic pathway more efficiently degrades refractory organic matter. However, Dauwe et al. (2001), proposed that differences between aerobic and anaerobic degradation are mainly related to absolute mineralization rates and do not necessarily depend on the lability of the organic matter.

Continental shelf sediments play an important role in the oceanic carbon cycle because most of the primary production occurs in coastal waters overlying continental shelves and slopes (e.g. Romankevich, 1984; Sorokin, 1983). The associated high organic carbon deposition rates through the water column combined with riverine contribution of terrestrial material are responsible for a relatively high organic input to shelf sediments.

In marine sediments with high organic carbon input such as continental shelf sediments, sulphate reduction is the most important anaerobic degradation pathway for oxidizing organic carbon, accounting for the greatest part of the oxidative and early diagenetic loss of organic carbon. Anaerobic degradation can account for greater than 50% of the total organic carbon oxidized in shelf sediments. Here, a large fraction of the organic carbon produced reaches the sea floor where it is buried and drives diagenesis. In

contrast, oxic (aerobic) respiration predominates in deep-sea sediments where most organic carbon is degraded while settling through the water column. Due to the enhanced level of primary production and high carbon loading, anaerobic mineralization processes are expected to be relatively important in sediments of the cores from the southwestern Black Sea shelf, with variations due to differences in organic carbon loading to the sediments, water depths and sedimentation rates.

Wijsman et al. (2002) have reported that early diagenetic processes in sediments of the continental shelf of the Black Sea are dominated by reduction due to diffusion of sulphate from the overlying sulphate-rich water into the sediments, and facilitated by low oxygen concentrations in the bottom water and high organic carbon deposition rates. Both aerobic and anaerobic degradation processes have been reported for organic carbon degradation in the Marmara Sea (Çağatay et al., 2004).

Similar moderate and constant TOC/TOC_{OR} ratios in the three Black Sea cores (Figure 4.13) on first observation suggest that there was moderate degradation of organic carbon in the cores before ~5000 yr BP. However, there appears to have been more degradation of organic carbon in core MAR00-8 judging from the higher biogenic opal and initial organic carbon contents in this core than in the other two. This interpretation is consistent with more shell-rich layers in core MAR00-8 and implies that sulphate reduction was moderately enhanced by the bioturbating action of fauna which brought sulphate into the sediments where it subsequently degraded the highly metabolizable (marine) organic matter that was initially present. However, the high sedimentation rate in this core (96 cm per 1000 yr; Aksu et al., 2002b) and rapid deposition probably means that not all the available marine organic matter that could have been metabolized was

consumed by sulphate reduction. Thus, part of the marine organic carbon escaped oxidation in the water column and at the sediment surface, accounting for the high TOC content for most of the 6400-5000 yr BP interval in core MAR00-8. In contrast, enriched TOC (>2%) values in sediments deposited before 5000 yr BP in core MAR00-6 does not necessarily indicate better organic carbon preservation, but rather that very little metabolizable (marine) organic matter was initially present as documented by high proportion of F_{TERR} and low amounts of biogenic opal during this time interval in the core. Thus, the more refractory terrestrial organic matter was, as expected, degraded less by sulphate reduction, accounting for enrichment in terrestrial organic carbon and a terrestrial isotopic signal in this time interval in the core.

However, in sediments deposited before 5000 yr BP in core MAR00-5 (except for a 5800 yr BP outlier) the general upward increase in TOC/TOC_{OR} ratios suggests increased diagenesis (a trend opposite to the observation in core MAR00-6) and enhanced oxidation of the sediments due to increasing oxygen supply to the sediments. Increased diagenesis and oxygen supply is also consistent with the presence of bivalves in the sediments, whose burrowing action would have also increased penetration of sulphate from the overlying seawater into the sediments to stimulate sulphate reduction. Although the degradation process likely degraded up to ~57% of the initial organic carbon in this core from 6400-5600 yr BP, it is not sufficient to explain the relatively low TOC values (<2%) in this time interval compared to the other Black Sea cores especially as relatively little metabolizable (marine) organic matter was initially present (as shown by the relatively low amount of biogenic opal and high F_{TERR} values). A plausible explanation is that either the moderately bioturbated sediments in this time interval were deposited

during periods of relatively high bottom water oxygen concentration (which would have encouraged acrobic degradation) and/or low surface productivities or both. In addition, the selectively preserved terrestrial organic carbon (relative to the marine fraction) might have also been subjected to oxidative degradation as a result of post-depositional aerobic oxidation (e.g. Prahl et al., 1997).

Subsequent increase in TOC to ~ 2% from 5400-5000 yr BP in core MAR00-5 is consistent with increased production inferred from the relatively high biogenic opal content and changing environmental conditions during deposition of these sediments to a low sulphate environment in which low microbial sulphate reduction occurred (as evidenced by paucity of shells, relatively high TOC/TOC_{OR} values and relatively heavier $\delta^{34}S$ values).

The general upward increase in TOC/TOC_{OR} ratios in core MAR00-6 for sediments younger than 5000 yr BP (Figure 4.15) suggests better preservation of organic carbon. This interpretation is inconsistent with the low sedimentation rate (15 cm per 1000 yr; Aksu et al., 2002b) observed for this core site, which should have promoted the degradation of the organic carbon. A plausible explanation for this contradiction is that only a small part of the organic matter (most likely the relatively small marine organic carbon fraction) was subjected to oxidative degradation by sulphate reduction (e.g. Pedersen and Calvert, 1990).

TOC enrichment in core MAR00-6 for sediments younger than 1000 yr BP is not only a matter of better preservation, but also due to higher productivity. This is supported by increased primary productivity (as evidenced by high biogenic opal contents), low sulphate reduction intensity (as shown by the low total sulphur contents and relatively

heavier $\delta^{34}S$ values), reduced salinity (C/S ratios between 5 and 6) and the poor oxygenation suggested earlier. These observations can be combined to reasonably conclude that the enhanced organic carbon preservation in these sediments (TOC/TOC_{OR} ~0.86) was due to low sulphate (and thus low microbial sulphate reduction) coupled with increased primary productivity and enhanced deposition of marine organic matter in an oxygen-deficient environment.

At first glance, the general upcore increase in TOC/TOC_{OR} ratios in the Marmara Sea core MAR98-11 (Figure 4.7) suggests reduced or weakening of organic carbon degradation through time and, therefore, better preservation. However, judging by the relatively low total sulphur contents and C/S values >3 after sapropel deposition around 6600 yr BP, the high TOC/TOC_{OR} values are more likely a reflection of reduction in organic carbon degradation by sulphate reduction as a result of progressively lower sulphate abundance rather than being the result of lowered productivity and/or oxygen depletion in the bottom waters. Although the sapropel sediments were deposited during conditions that were open with respect to sulphate (inferred from the relatively lighter $\delta^{34}S$ values; Passier et al., 1996a, 1997; Goldhaber and Kaplan, 1974, 1988), there is restriction of the diffusion of sulphate into these dark gray sediments. This hypothesis is supported by the earlier observation of anoxic conditions inferred from the presence of millimetre scale lamination accentuated by color banding, since laminated sediments have lower permeability than bioturbated sediments.

Absence of bioturbation structures (mottling), shells or shell fragments in sediments younger than 6400 yr BP (which corresponds to the upper 108 cm interval in core MAR98-12) is also consistent with the high TOC/TOC_{OR} ratios (i.e. high degree of

organic matter preservation). The bioturbation structures would have enhanced the oxic degradation of organic matter by increasing oxygen supply (Davis 1974; Andersen and Jensen, 1991) and/or would have promoted the penetration of sulphate from seawater into the sediments to stimulate bacterial sulphate reduction. Thus, variations in primary production rather than depleted bottom water oxygen content most likely exerted a strong control on organic carbon preservation in core MAR98-11 for sediments younger than 6400 yr BP.

This hypothesis is corroborated by the fact that most of these sediments, which are characterized by a relatively high degree of organic carbon preservation, roughly correspond to time intervals with the highest biogenic opal values and/or lowest F_{1ERR} values. They also have a high variability in the $\delta^{34}S$ values and color gradations from light olive gray to darker olive gray back to light, which suggest fluctuations between oxic and low-oxygen conditions of the bottom waters, due likely to either the temporary development of suboxic conditions and/or the onset of reventilation at the end of sapropel deposition. This interpretation is in agreement with previous studies (e.g. Kaminski et al., 2002; Aksu et al., 2002a) which propose that, by ~6400 yr BP, the inflow of Mediterranean water into the Marmara Sea via the Aegean Sea began to exceed the Black Sea brackish outflow, resulting in a progressive increase in ventilation and in bottom water oxygenation, although a return to fully oxygenated conditions did not occur.

4.6 Plausible Paleoenvironmental Implications

On the basis of the geochemical data and trends discussed previously, it is possible to propose a general scenario for paleoenvironmental conditions during sediment and sapropel deposition in the studied cores in relation to late Quaternary changes in the

sea-level, salinity, organic matter inputs, oxygen availability and consumption, water column stratification, and sulphate reduction. For this paleoenvironmental interpretation, it is necessary to consider the significant depositional changes that occurred in both the Black and Marmara seas after the last glacial maximum. Paleoceanographic events associated with the last glacial-interglacial transition in the Black and Marmara seas are believed to have been controlled by oscillations in both regional and global sea levels, and by climatic variations. Together, these changes had important paleoenvironmental implications for the source(s) of organic matter and its subsequent preservation, for the mechanism(s) of sapropel formation, and for interaction(s) between the Black Sea and the Mediterranean Sea via the intervening Marmara Sea.

An attempt will be made to explain the paleoenvironmental implications of findings from this study by integrating these new data with previously published observations from the Black and Marmara Seas. In order to develop a general sequence of climatic changes, dated ^{14}C intervals are assumed to represent periods of uniform deposition. Furthermore, accumulation rates are assumed to be constant for each core, so changes in organic carbon concentrations will be interpreted as changes in organic carbon flux to each core site. A more accurate assessment of fluxes will only be possible if several additional ^{14}C dates are obtained for each core.

Although this simplification might reduce the accuracy of the paleoenvironmental interpretation, it does not affect the interpretation of the general pattern of climate changes that occurred in the study area during the Holocene in the Black Sea cores and the last Glacial Maximum in the Marmara Sea core. Correlation between climate and

oceanographic changes and dated events will he considered as giving a general framework for these concurrences rather than providing an explanation for particular events.

4.6.1 Impacts of sea level variations and climate changes

The history of the hydrological regime of the Black Sea is punctuated by fluctuations in its water level and salinity, which have directly or indirectly heen modulated by different climate-related events in the past and by oscillations in the halance between evaporation, river input and precipitation. Quaternary transgression due to sea-level rises and regressions due to sea-level falls (Tchepalyga, 2002) have been associated with interglacial and glacial times, respectively. The transgressions are widely believed to have resulted from a combination of melting ice sheets in central-eastern Europe and central Asia, wet periods with increased precipitation, and reduced evaporation during cooler time intervals. The regressions, on the other hand have resulted mostly from increased evaporation and low global sea level (Yaltlrak et al., 2002).

Although various authors have provided plausible explanations, there is still no general consensus on the synchronization of Black Sea water levels and global eustatic sea-level changes. However, according to the calibrated global sea level curve shown in Figure 4.34, global sea level rose to the sill depths of the Straits of Dardanelles and Bosphorus at ~12,000 and ~9500 yr BP respectively. Furthermore, according to recent studies (e.g. Aksu et al., 2002a; Kaminski et al., 2002), sea level in the Black Sea rose to −40 m by ~10 ka, after which continued sea-level rise stalled until ~9 ka as the Black Sea began to spill across the Bosphorus Strait into the Marmara Sea. It was not until the uninterrupted outflow became weaker and global sea level attained the Black Sea level

that saline Mediterranean deep water started to cross the Bosphorus Strait, initiating a two-way flow in that channel.

The data collected from the Black Sea cores in this thesis demonstrate marine and brackish transitions during sea level changes. The mix of brackish-water sediments with more marine sediments suggests deposition during a transgression. This is consistent with periods of sea-level rise that have been reported by Kaplin and Selivanov (2004) as occurring in the Black Sea in the middle and late Holocene (7500 yr BP, 7000-6000 yr BP, 5500-4500 yr BP and 2200 – 1700 yr BP) after the incursion of Mediterranean waters.

Organic matter input into the sediments changed with these changes in salinity, sea level, oxygen content of the bottom waters and changes in depositional conditions, leading to the observed variability in sedimentological geochemical characteristics of the Black Sea cores. Those differences in the TOC content of the Black Sea cores that correlate with modern water depth suggest different modes of organic preservation with increasing water depth along the southwestern Black Sea shelf. This is a valid hypothesis because modern water depth is <15m higher than paleo water depth over the period 7000-0 yr BP (Figure 4.31). The most organic-rich sediments in the Black Sea cores studied for this thesis were deposited at the relatively deeper core MAR00-6. For sediments >5000 yr BP, the relatively higher TOC contents in core MAR00-6 compared to the other Black Sea cores can be explained by better preservation of organic matter due to the existence of a more stable water-column well below wave base. Alternatively, there may have been a greater salinity contrast between surface and bottom waters at this site before 5000 yr BP.

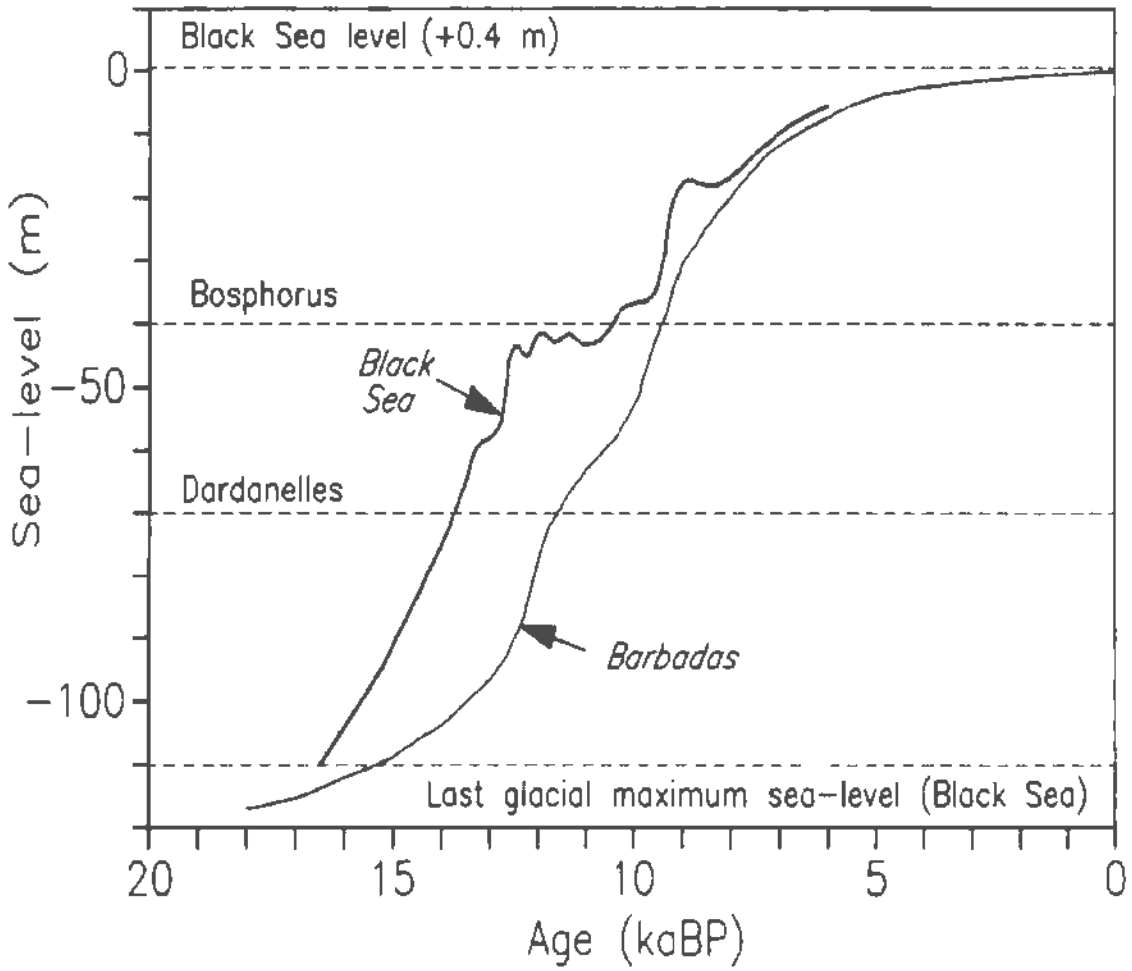


Figure 4.31: Calibrated post-glacial sea–level curve for the Black sea. The Barbados curve is the global curve of Fairbanks (1989). 1 kaBP = 1000 yr BP. Diagram modified from Aksu et al. (2002a; Fig. 24).

In the shelf core MAR00-5, however, the relatively lower TOC values correlate with an increased input of terrigenous organic carbon (F_{TERR}) and reduced biogenic opal values. These indicators likely reflect greater continental runoff in this core before 5000 yr BP. The predominantly terrigenous source of this organic matter is supported by its carbon isotopic values. The explanation of increased runoff is in agreement with the suggestion of Arthur and Dean (1988) that coincident depleted $\delta^{13}C$ values and low TOC flux in sediments from the southwestern Black Sea signifies high freshwater runoff to the basin. The TOC contents of the relatively deeper cores MAR00-6 and MAR00-8 are higher than in the near shore core MAR00-5 probably because little marine organic matter reached the MAR00-5 core site, or because of a stronger degradation of marine organic matter closer to shore

After ~5000 yr BP, sediments were deposited when the sea level had essentially reached its present level (Figure 4.31). There is a relatively increased marine input for core MAR00-6 in sediments deposited after ~5000 yr BP, which is likely due to a weakened Black Sea outflow much after the establishment of two-way flow across the Bosporus strait believed to have occurred ~8400 yr BP. The weakened brackish outflow is also consistent with a progressive increase in bottom water oxygenation and the establishment of more fully marine conditions. This marine influx produced a progressive shift to marine values in most proxies, particularly in core MAR00-6 with its longer sedimentary record. There were progressively smaller amounts of terrestrial organic matter and larger amounts of marine organic matter upwards after ~6400 yr BP.

Fluctuations in the C/S data indicate varying environmental conditions from non-reducing to suboxic and then to anoxic (sulphate reducing). Alternation of bioturbated

and laminated sediments in core MAR00-6 exemplifies how the water column in the Black Sea evolved from predominantly oxic conditions in the early part of the Holocene to anoxia at present (Arthur and Dean 1998). In addition, the observed shift in dominance from terrestrial- to marine-derived organic carbon and fluctuating sulphidic and non-sulphidic depositional conditions after ~5000 yr BP, might reflect increased aridity.

According to results presented by Aksu et al., (1995a) from benthic foraminifera, during the early Holocene from 9600 to 6400 yr BP in the Aegean Sea, there was continuous southward discharge of Black Sea surface waters. During this period the Black Sea outflow to the Marmara Sea was so strong that there was little or no northward penetration of Mediterranean water (Aksu et al., 1999). This resulted in the formation of a low salinity lid which further enhanced stratification of the water column, prevented vertical mixing and caused very low oxygen concentrations in the bottom waters of the Aegean and Marmara seas. A prerequisite for maintaining the low salinity lid during the Holocene warming was increased humidity.

However, with decreased outflow from the Black Sea after ~6400 yr BP (Aksu et al., 2002a; Kaminski et al., 2000) and a subsequent climatic shift to a period of cooler, drier climate between ~5000–2000 yr BP in the Black Sea (Mudie et al., 2002), there would have been a cooling of the low-salinity surface layer. This change in climatic condition might have resulted in the stratified water column becoming periodically unstable, allowing greater mixing of surface and deep waters. This would provide an explanation for the change to suboxic conditions observed in core MAR98-11 and which previous studies have shown to be persistent to the present in the Marmara Sea (Aksu et al., 2002a, Kaminski et al., 2002).

4.6.2 Implications for Sapropel Deposition

4.6.2.1 Black Sea Cores

The relatively high TOC_{OR} values of sediments deposited between ~7200 and 5400 yr BP in all three Black Sea cores corresponds with the development of water column anoxia which is believed to be synchronous across the Black Sea basin at ~7500 yr BP (Arthur and Dean., 1988). This development was likely the result of the spill over of saline Mediterranean waters through the Bosporus Strait and the establishment of two–way flow at ~ 8400 yr BP. The denser salt water from the Mediterranean caused greater stratification in the Black Sea and sapropel deposition in Unit II of the Black Sea (Arthur and Dean 1988).

The contrasting sapropel thicknesses and variations in duration of sapropel deposition in the Black Sea cores can either be explained by variations in depth and/or post-depositional oxidation, which removed sufficient carbon to prevent the formation of sapropel (e.g. De Lange et al., 1989). In cores MAR00-5 and MAR00-8, a relatively shallow water depth together with evidence of bioturbation of the black and gray sediments suggests that abundant organic-matter production rather than stagnant bottom waters was the most probable cause of sapropel formation. In core MAR00-6 sediments deposited before 5000 yr BP, sapropel deposition was most likely controlled by marine productivity and the change to a drier and cooler climate with diminished runoff from the land (middle Holocene cooling; Artizegui et al., 2000). It however remains unclear from the proxy data whether oxygenated and dysaerobic bottom-water conditions prevailed during deposition of the sediments.

An exception is in the late Holocene sediments from ~5000 yr BP to the present in core MAR00-6. The absence of burrows in these TOC-rich laminated sediments in the upper part of core MAR00-6 suggests that during a period of increased marine productivity, oxygen in the water column was consumed as organic matter settled to the bottom, possibly rendering the lower portions of the water column anoxic. This interpretation conforms to earlier suggestions that anoxic conditions are a necessary requirement for deposition of the laminated, unburrowed muds.

4.6.2.2 Marmara Sea Core MAR98-11

Radiocarbon dates correlated to core MAR98-11 from a nearby core site place sapropel M1 deposition between ~9800 and ~6600 yr BP. Sapropels S1 and M1 formed contemporaneously in the Mediterranean and Marmara seas, respectively (Çağatay et al., 2002; Aksu et al., 2002a). Sapropel deposition in the core began when the water level in the Black Sea rose to breach the Bosphorus Strait and its brackish-water began to flow across the straits into the Marmara Sea. According to Aksu et al. (2002a), this required that the Black Sea level was at ~ -40 m or shallower by ~10000 yr BP, when the elevation of the global ocean was still lower than the Black Sea level (Figure 4.31). Sea-level rise in the Black Sea then stalled until ~9000 yr BP when the global ocean level reached the Black Sea level; subsequently, both water bodies rose in tandem.

The relatively high terrestrial organic-carbon component at the onset of sapropel deposition at ~9800 yr BP in core MAR98-11 suggests significant increases in the flux of terrestrial organic material. Hiscott and Aksu (2002) and Abrajano et al. (2002) attribute this increased flux to an increased input of Black Sea brackish water. Further evidence

for this outflow comes from the coincidence of ^{13}C-depleted isotopic values and increased terrestrial contribution (from the mixing equation) from ~9800 to ~6600 yr BP. The ^{13}C-depleted terrestrial material was provided by large rivers entering the Black Sea since the Marmara Sea itself has limited fluvial input from local rivers. The brackish-water outflow likely resulted in density stratification and reduced oxygen levels in the bottom waters during sapropel deposition. The sapropel formation ended at ~ 6600 yr BP just before there was a reduction in the Black Sea brackish-water outflow through the Bosporus Strait and a strengthening in the northward penetration to the Black Sea of saline Mediterranean waters from the Aegean Sea. The reduced outflow and greater mixing caused a progressive increase in bottom water oxygenation and the establishment of more marine conditions.

4.6.3 Connection between the Black Sea and the Mediterranean Sea (via the Marmara Sea)

Different hypotheses have been proposed for the direction and timing of the connection between the Black Sea and the Mediterranean Sea. Ryan et al. (1997) and Ryan and Pitman (1998) had earlier proposed a catastrophic Holocene marine flooding of the Black Sea with saline waters from the Mediterranean Sea at ~7500 yr BP, referred to by Aksu et al. (2002a; GSA Today) as the "*Flood Hypothesis*". This hypothesis was subsequently modified by Ryan et al. (2003a, b) to suggest that there was an evaporation-driven drawdown of the level of the Black Sea based on their interpretation of climatic events from the Caspian-Black Sea region during the Quaternary. The revised hypothesis suggested that there were "two pulses of outflow from the Black Sea to the world ocean" at ~16000–14700 yr BP and ~11000–10000 yr BP and that the date for the catastrophic

marine flooding of the Black Sea took place earlier at ~8400 yr BP. Between these pulses, the Black Sea is claimed to have fallen twice from 14700-11000 yr BP and from ~10000–8400 yr BP as a result of the excess evaporation (Ryan et al., 2003a). The latter interpretation was supported by the evidence from strontium isotopes and the recognition of a Black Sea shoreline that was "well below a shallow Bosphorus sill depth", which they believed to have developed between ~10000 and 8400 yr BP.

Other investigators (e.g. Aksu et al., 1995; Aksu et al., 1999; Çağatay et al., 2000; Aksu et al., 2002 a, b, c; Kaminski et al., 2002); and Abrajano et al., 2002, amongst others) using proxy indicators in sediment cores have argued for a sustained brackish outflow from the Black Sea to the Mediterranean Sea via the intervening Marmara Sea since ~10000 yr BP, or earlier. This hypothesis was named the "*Outflow Hypothesis*" by Aksu et al. (2002a).

The only points of agreement between the two hypotheses are that there was a connection between the Black Sea and the Marmara Sea from ~11000-10000 yr BP and since ~8400 yr BP. Disparate reasons that have been given for the mechanisms and processes (such as the sill depths, continental runoff and evaporation) involved in connecting the two water bodies still remain controversial. Unlike the marine deluge put forward by proponents of the Flood Hypothesis, Aksu et al. (2002b) and other proponents of the Outflow Hypothesis believe that the delayed reconnection of the Black Sea and the Mediterranean Sea that took place at ~8000 yr BP, well after the former had risen to the Bosporus bedrock sill depth of ~40 m at ~11000–10000 yr BP (Figure 4.31). This delay was in part because of the time lag involved in developing two-layer flow (Lane-Serff et al., 1997).

Although lines of evidence discussed above suggest that the study area for this thesis was subjected to short-term climatic changes and fluctuations of sea level that influenced salinity distribution, productivity and preservation, it is not possible from available data in this thesis to argue for or against the *Flood Hypothesis* or *Outflow Hypothesis*. This is because the Black Sea cores here do not extend back to 8400 yr BP, which is the proposed date of the catastrophic flood. Data in this thesis from the Marmara Sea (core MAR98-11) broadly supports the *Outflow Hypothesis*.

Chapter 5 - Summary and Recommendations

5.1 Summary

Organic matter input into sediments is modulated by changes in salinity, sea level, oxygen content of the bottom waters, and changes in depositional conditions, leading to the observed variability in sedimentary geochemical characteristics of the three cores examined in this thesis.

Linear extrapolations based on ^{14}C dates in the three Black Sea cores indicate that while MAR00-6 is characterized by continuous and uniform sediment deposition, cores MAR00-5 and MAR00-8 lack a record of the last ~5000 years. Lithostratigraphic correlation to nearby core MAR98-12, with its ^{14}C dates, places sapropel deposition in the Marmara Sea core MAR98-11 between ~9800 to ~6600 yr BP.

The range of $\delta^{13}C$ values from ~-26‰ to ~-23‰ for the TOC in the Black Sea cores was interpreted in terms of mixing of isotopically light land-derived material with isotopically heavier autochthonous carbon derived from primary marine production. There is, however, a higher contribution from land-derived sources to the TOC content in the relatively deeper core MAR00-6. Differences in the TOC content of the Black Sea cores that correlate with modern water depth suggest different modes of organic preservation with increasing water depth along the southwestern Black Sea shelf. For sediments older than ~5000 yr BP, the relatively higher TOC contents in core MAR00-6 compared to the other Black Sea cores can be explained by better preservation of organic matter beneath a more stable stratified water-column well below wave base. In addition, because the core sites MAR00-5 and MAR00-8 are in relatively shallower water depths where burrowing and oxygenation would have been greater, their sediments have been

more susceptible to diagenetic effects. Alternatively, there might have been a greater salinity contrast between surface and bottom waters at this site before ~5000 yr BP. Changes in the delivery and relative contribution of land-derived organic matter, coupled with a relatively constant contribution from marine sources, controlled the organic carbon content in core MAR00-6 sediments deposited after ~5000 yr BP.

Fluctuations in the C/S data for the Black Sea cores indicate varying environmental conditions (from non-reducing to suboxic and then to anoxic (sulphate reducing)). These fluctuations exemplify how the water column in the Black Sea evolved from predominantly oxic conditions in the early part of the Holocene to anoxia today (Arthur and Dean 1998). In addition, the observed shift in dominance from terrestrial- to marine-derived organic carbon and fluctuating sulphidic and non-sulphidic depositional conditions after ~5000 yr BP might reflect increased aridity and diminished runoff.

There are contrasting sapropel thicknesses and variations in duration of sapropel deposition in the Black Sea cores. In cores MAR00-5 and MAR00-8, a relatively shallow water depth together with evidence of bioturbation of the black and gray sediments suggests that abundant organic-matter production rather than stagnant bottom waters was the most probable cause of sapropel formation. In those sediments in core MAR00-6 deposited before ~5000 yr BP, sapropel deposition was most likely controlled by increased marine productivity and diminished runoff from the land.

Data in this thesis from the Black Sea cores demonstrate marine to brackish transitions during sea-level changes. The passage from brackish-water sediments to more marine sediments suggests deposition during a transgression. This is consistent with sea-

level rise that occurred in the Black Sea in the middle and late Holocene after the incursion of Mediterranean waters.

Considerable scatter in the TOC-TS cross plot for Marmara Sea core MAR98-11 is probably the result of variations in total sulphur content and depositional conditions. Sediments are grouped into three categories based on how they plot on the TOC-TS plot. Sapropel deposition from ~9800 to ~6600 yr BP in the Marmara Sea core MAR98-11 coincides with the contemporaneous sapropel S1 in the Aegean Sea. $\delta^{13}C$ values and the relatively high terrestrial organic-carbon component during this period point to a predominantly terrestrial source for the organic matter. This increase in the flux of terrestrial organic material is attributable to an increased input of Black Sea brackish water that started ~11000 to 10500 yr BP. Sapropel formation ended at ~ 6600 yr BP just before there was a reduction in the Black Sea brackish-water outflow through the Bosphorus Strait and a strengthening in the northward penetration to the Black Sea of saline Mediterranean waters from the Aegean Sea. The reduced outflow and greater mixing caused a progressive increase in bottom water oxygenation and the establishment of more marine conditions.

Data from the Marmara Sea core MAR98-11 broadly supports the *Outflow Hypothesis* of Aksu et al. (2002a). Those authors argue for a sustained brackish outflow from the Black Sea to the Mediterranean Sea since ~11000–10500 yr BP. The brackish-water outflow likely resulted in density stratification and reduced oxygen levels in the bottom waters during sapropel deposition in the Marmara Sea.

5.2 Recommendations for Future Work

Assumptions about the end-member $\delta^{13}C$ source values for marine and terrestrial organic carbon might have resulted in errors in estimating the contributions from these sources. Therefore, the proportions of terrestrial- versus marine-sourced organic matter in the sediments should be evaluated further on the basis of petrographic and Rock Eval data. Further analysis and comparison of other proxy indicators of productivity (e.g. Ba/Al) and denitrification ($\delta^{15}N$) in the studied sediments as well as the combined use of several geochemical proxies (C/N and $\delta^{15}N$) could be used to test for diagenetic effects in the sediments so as to improve confidence in the interpretation of the data. The geochemistry of redox-sensitive trace elements in the cores, such as Cd, Cu, U, Mo, V and Re measured by ICP-MS, would help provide further insight into the variability in water column redox conditions and sediment redox state. These would bolster ideas derived from the simple use of C/S ratios.

Further studies are needed (especially in the ~10000 to 7000 yr BP time interval) on the influence and effects of fluctuations in the level of the Black Sea and adjacent seas (e.g., Caspian Sea). Older core material must be analyzed from the Black Sea than what was available for this thesis. This might provide important clues in resolving the disputed events between the *Flood Hypothesis* and the *Outflow Hypothesis* and lead to a better understanding of the communication between the Black Sea and eastern Mediterranean.

While there seems to be a lot of seismic, micropaleontological, stable isotopic and sedimentological evidence from proponents of both the *Flood Hypothesis* and the *Outflow Hypothesis* to bolster their respective arguments, there has not been much detailed work or arguments from the organic geochemical point of view, with the

exception of a preliminary study by Abrajano et al. (2002). A more extensive and detailed study using molecular organic geochemical techniques would further characterize the distribution, quantity and quality of organic matter, its conditions of formation and preservation, nutrient supply and conditions in the depositional environment. Such data on cores extending to >8400 yr BP would augment the preliminary observations made in this study and provide detailed insights into paleoenvironmental changes that caused high organic matter deposition in the study area.

Using biomarker analysis, the bulk and compound-specific $\delta^{13}C$ records from different study sites within the basin could potentially be correlated at a high-resolution scale, resulting in significant enhancement of the stratigraphic resolution, especially for the shallow water core sites. The precise analysis of long chain n-alkanes, indicating higher land plants, could quantify river input into the basin, while carbon isotope composition of these alkanes might provide evidence for vegetation transitions between C4/C3 land plants during periods of sapropel and non-sapropel formation. Biomarker-derived parameters can also indicate changes in primary productivity conditions, depletion of water-column oxygen content, and changes in sediment provenance in response to sea-level changes.

Finally, a much greater number of radiocarbon dates will be required to fully quantify accumulation rates, so that actual fluxes of marine and terrestrial organic carbon to the environment can be assessed. For this thesis, the age models required too many assumptions for a precise temporal analysis to be completed.

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CHARACTERIZATION OF CORES FROM THE BLACK AND MARMARA SEAS: IMPLICATIONS FOR TOC SOURCE AND PRESERVATION AND POTENTIAL FOR PALEOENVIRONMENTAL INTERPRETATION

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